



## 【特許請求の範囲】

【請求項1】排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態で $\text{NO}_x$ を化学吸着し、酸化剤に対し還元剤が同量以上の状態で吸着した $\text{NO}_x$ を接触還元する $\text{NO}_x$ 吸着触媒を排ガス流路に配置し、排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態をつくらせて吸着触媒上に $\text{NO}_x$ を化学吸着させ、次に酸化剤に対し還元剤が同量以上の状態をつくり、吸着触媒上に吸着した $\text{NO}_x$ を還元剤と接触反応させて $\text{N}_2$ に還元して無害化する、内燃機関の排ガス浄化装置において、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項2】少なくともカリウム（K）、ナトリウム（Na）、マグネシウム（Mg）、ストロンチウム（Sr）及びカルシウム（Ca）から選ばれる一種以上の元素を成分の一部として含む $\text{NO}_x$ 吸着触媒を排ガス流路に配置し、排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態をつくらせて吸着触媒上に $\text{NO}_x$ を化学吸着させ、次に酸化剤に対し還元剤が同量以上の状態をつくり、吸着触媒上に吸着した $\text{NO}_x$ を還元剤と接触反応させて $\text{N}_2$ に還元して無害化する、内燃機関の排ガス浄化装置において、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項3】少なくともカリウム（K）、ナトリウム（Na）、マグネシウム（Mg）、ストロンチウム（Sr）及びカルシウム（Ca）から選ばれる一種以上の元素を成分の一部として含む $\text{NO}_x$ 吸着触媒を排ガス流路に配置し、酸化還元化学量論関係においてHC等の還元剤に対して $\text{O}_2$ 等の酸化剤が多い状態をつくらせて吸着触媒表面及び表面近傍に $\text{NO}_x$ を化学結合により捕捉し、次に酸化剤に対し還元剤が同量かもしくは多い状態をつくり、吸着触媒に捕捉された $\text{NO}_x$ を還元剤と接触反応させて $\text{N}_2$ に還元して無害化する、内燃機関の排ガス浄化装置において、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項4】請求項1及び2において、カリウム（K）、ナトリウム（Na）、マグネシウム（Mg）、ストロンチウム（Sr）及びカルシウム（Ca）から選

ばれる少なくとも一種とセリウム等からなる希土類から選ばれる少なくとも一種と、白金、ロジウム、パラジウム等からなる貴金属から選ばれる少なくとも一種の元素を含む、金属および金属酸化物（もしくは複合酸化物）からなる組成物もしくは該組成物を多孔質耐熱性金属酸化物に担持してなる組成物を吸着触媒として用いた内燃機関の排ガス浄化装置において、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項5】請求項1及び2において、カリウム（K）、ナトリウム（Na）、マグネシウム（Mg）、ストロンチウム（Sr）及びカルシウム（Ca）から選ばれる少なくとも一種と、セリウム等からなる希土類から選ばれる少なくとも一種と、白金、ロジウム、パラジウム等からなる貴金属から選ばれる少なくとも一種と、チタン及びシリコンから選ばれる少なくとも一種の元素を含む、金属および金属酸化物（もしくは複合酸化物）からなる組成物、該組成物を多孔質耐熱性金属酸化物に担持してなる組成物を吸着触媒として用いた内燃機関の排ガス浄化装置において、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項6】請求項1から5において、自動車の駆動軸トルクまたは内燃機関の出力トルクが変動しないような関係で内燃機関に吸入される空気量、燃料量、点火時期、燃料噴射時期、変速機の変速比、エンジン回転数のいずれかの組み合わせの制御量で制御することを特徴とする排気浄化制御装置。

【請求項7】請求項1から5において、触媒の被毒物を触媒から排除する処理を所定の期間毎、自動車の所定走行距離毎、吸入空気量、燃料供給量、排気量のいずれかの積算値が所定値に達する毎のいずれかで実施することを中心とする排気浄化装置。

【請求項8】請求項1から5において、触媒の被毒物を触媒から排除する処理を $\text{NO}_x$ 吸着能力の劣化度が所定値以上超えた時に実施することを特徴とする排気浄化装置。

【請求項9】請求項1から5において、内燃機関に供給する燃料を増量し、排気管に空気を導入することにより排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項10】請求項9において、点火時期の遅角制御

を組み合わせるにより排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することを特徴とする排気浄化制御装置。

【請求項 11】請求項 9 から 10 において、触媒の被毒物を触媒から排除する処理を所定の期間毎、自動車の所定走行距離毎、吸入空気量、燃料供給量、排気量のいずれかの積算値が所定値に達する毎のいずれかで実施することを特徴とする排気浄化装置。

【請求項 12】請求項 9 から 10 において、触媒の被毒物を触媒から排除する処理を  $\text{NO}_x$  吸着能力の劣化度が所定値以上超えた時に実施することを特徴とする排気浄化装置。

#### 【発明の詳細な説明】

##### 【0001】

【発明の属する技術分野】本発明は自動車等の内燃機関から排出される排気ガスを浄化する装置に係わり、特に希薄空燃比（リーンバーン）で運転可能な内燃機関及び該内燃機関を搭載した自動車から排出される排ガスの浄化装置に関する。

##### 【0002】

【従来の技術】自動車等の内燃機関から排出される排ガスに含まれる、一酸化炭素（ $\text{CO}$ ）、炭化水素（ $\text{HC}$  : Hydrocarbon）、窒素酸化物（ $\text{NO}_x$ ）等は大气汚染物質として人体に悪影響を及ぼす他、植物の生育を妨げる等の問題を生起する。そこで、従来より、これらの排出量低減には多大の努力が払われ、内燃機関の燃焼方法の改善による発生量の低減に加え、排出された排ガスを触媒等を利用して浄化する方法の開発が進められ、着実な成果を挙げてきた。ガソリンエンジン車に関しては、三元触媒なる  $\text{Pt}$ 、 $\text{Rh}$  を活性の主成分とし、 $\text{HC}$  及び  $\text{CO}$  の酸化と  $\text{NO}_x$  の還元を同時に行って無害化する触媒を用いる方法が主流となっている。

【0003】ところで、三元触媒はその特性から、ウィンドウと称される理論空気燃料比近傍で燃焼させて生成した排ガスにしか効果的に作用しない。そこで従来は、空燃比は自動車の運転状況に応じて変動するものの変動範囲は原則として理論空燃比（ガソリンの場合  $A/F$ （空気の重量）/  $F$ （燃料の重量）= 約 14.7 ; 以下本明細書では理論空燃比を  $A/F = 14.7$  で代表させるが燃料種によりこの数値は変る。）近傍に調節されてきた。しかし、理論空燃比より希薄（リーン）な空燃比でエンジンを運転できると燃費を向上させる事ができることから、リーンバーン燃焼技術の開発が進められ、最近では空燃比 18 以上のリーン域で内燃機関を燃焼させる自動車が増えている。しかし前述の様に現用三元触媒でリーンバーン排気の浄化を行わせると  $\text{HC}$ 、 $\text{CO}$  の酸化浄化は行えるものの  $\text{NO}_x$  を効果的に還元浄化することはできない。したがって、リーンバーン方式の大型車への適用、リーンバーン燃焼時間の拡大（リーンバーン方式の

適用運転域の拡大）を進めるには、リーンバーン対応排ガス浄化技術が必要となる。そこでリーンバーン対応排気浄化技術、すなわち酸素（ $\text{O}_2$ ）が多量に含まれる排ガス中の  $\text{HC}$ 、 $\text{NO}$ 、 $\text{NO}_x$  を浄化する技術の開発、特に  $\text{NO}_x$  を浄化する技術の開発が精力的に進められている。

【0004】特開昭 63-61708 号では、リーンバーン排ガスの上流に  $\text{HC}$  を供給し、排ガス中の  $\text{O}_2$  濃度を触媒が有効に機能する濃度域まで低め触媒の能力を引き出す方法が提案されている。

【0005】特開昭 62-97630 号、62-106826 号、62-117620 号は排ガス中の  $\text{NO}_x$  を（ $\text{NO}$  は酸化して吸収され易い  $\text{NO}_2$  に変換した後） $\text{NO}_x$  吸収能を有する触媒と接触させて吸収除去し、吸収効率が低下した時点で排ガスの通過を止めて  $\text{H}_2$ 、メタン・ガソリン等の  $\text{HC}$ 、等の還元剤を用いて蓄積された  $\text{NO}_x$  を還元除去し、触媒の  $\text{NO}_x$  吸収能を再生する方法が示されている。

【0006】また、 $\text{PCT}/\text{JP}92/01279$  及び  $\text{PCT}/\text{JP}92/01330$  には、排ガスがリーンの時に  $\text{NO}_x$  を吸収し排ガス中の酸素濃度を低下させると吸収した  $\text{NO}_x$  を放出する  $\text{NO}_x$  吸収剤を排気通路に設置し、排気ガスがリーンのときに  $\text{NO}_x$  を吸収させ、吸収させた  $\text{NO}_x$  を  $\text{NO}_x$  吸収剤に流入する排ガス中の  $\text{O}_2$  濃度を低下せしめて放出させる、排気浄化装置が提案されている。

【0007】しかし、特開昭 63-61708 号において触媒が機能する空燃比である（ $A/F$ ）14.7 程度に相当する排ガスの組成（ $\text{O}_2$  濃度約 0.5 % 程度）を達成するには多量の  $\text{HC}$  が必要となる。同発明のブローバイガスの利用は有効であるものの、内燃機関運転中の排ガスを処理するに十分な量ではない。燃料を投入することも技術的には不可能ではないが、リーンバーン方式で節減した燃費を低下させる結果となる。

【0008】また、特開昭 62-97630 号、62-106826、62-117620 号では、 $\text{NO}_x$  吸収剤の再生にあたり排ガスの流通を停止して  $\text{HC}$  等の還元剤を  $\text{NO}_x$  吸収剤に接触させるため、還元剤の排ガス中の  $\text{O}_2$  による燃焼消費が大幅に抑制されて還元剤の使用量が激減する。しかし、 $\text{NO}_x$  吸収剤を 2 つ設け、且つ、排ガスをこれらに交互に流通させるための排気切り替え機構が必要で、排気処理装置の構造が複雑になることは否定できない。

【0009】さらに、 $\text{PCT}/\text{JP}92/01279$  及び  $\text{PCT}/\text{JP}92/01330$  では、排ガスを常時  $\text{NO}_x$  吸収剤に流通させておき、排ガスがリーンの時に  $\text{NO}_x$  を吸収させ、排ガス中の  $\text{O}_2$  濃度を低下させて吸収した  $\text{NO}_x$  を放出させて吸収剤を再生するため、排ガス流の切り替えは不要で、上記方式の問題点は解消する。しかし、以上の触媒は排気に硫黄（ $\text{SO}_x$ ）が含まれていると  $\text{NO}_x$  吸収剤が  $\text{SO}_x$  と化合して硫化物となり、吸収能力が急速に劣るといった問題があった。

## 【0010】

【発明が解決しようとする課題】本発明は、上記従来技術の問題点に鑑み、排気処理装置の構造が簡単であり、且つ、還元剤の消費量が少なく、且つ、耐久性に優れた、内燃機関のリーンバーン排ガスからNO<sub>x</sub>等の有害成分を効果的に除去・無害化できる排気浄化制御装置を提供することにある。

## 【0011】

【課題を解決するための手段】上記課題は、内燃機関から排出される排気を理論空燃比もしくは燃料過剰（リッチ）の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物（SO<sub>x</sub>）を触媒から排除することで劣化したNO<sub>x</sub>吸着能力を回復させて、解決することができる。以下にNO<sub>x</sub>吸着触媒についてのNO<sub>x</sub>吸着、還元方法について説明するが、このNO<sub>x</sub>吸着能力は排気に含まれる硫黄分（SO<sub>x</sub>）の触媒への蓄積量にともなって劣ってくる。

【0012】本発明に使用されるNO<sub>x</sub>吸着触媒では、排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態でNO<sub>x</sub>を化学吸着し、酸化剤に対し還元剤が同量以上の状態で吸着したNO<sub>x</sub>を接触還元するNO<sub>x</sub>吸着触媒を排ガス流路に配置し、排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態をつくらせて吸着触媒上にNO<sub>x</sub>を化学吸着させ、次に酸化剤に対し還元剤が同量以上の状態をつくり、吸着触媒上に吸着したNO<sub>x</sub>を還元剤と接触反応させてN<sub>2</sub>に還元して無害化する。

【0013】ここで吸着触媒は、NO<sub>x</sub>等の物質を吸着する能力を持ち同時に触媒機能を持つ材料を指す。本発明では、NO<sub>x</sub>を吸着して捕捉する能力とNO<sub>x</sub>を接触的に還元する能力及びHC、CO等を接触的に酸化する能力を持つ材料を指す。

【0014】また、酸化剤はO<sub>2</sub>、NO、NO<sub>2</sub>等として酸素である。還元剤は、内燃機関に供されたHC、燃焼仮定で生成するその派生物としてHC（含む含酸素炭化水素）、CO、H<sub>2</sub>等、さらには、後述の還元成分として排ガス中に添加されるHC等の還元性物質である。

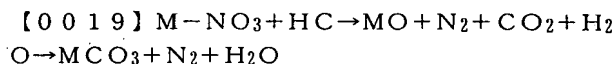
【0015】前述のように、リーン排ガスとNO<sub>x</sub>を窒素にまで還元するための還元剤としてのHC、CO、H<sub>2</sub>等とを接触させるとこれらは排ガス中の酸化剤としてのO<sub>2</sub>と燃焼反応を起こす。NO<sub>x</sub>（NO及びNO<sub>2</sub>）もこれらと反応して窒素に還元される。通常は両反応が平行して進行するため酸素の共存下では還元剤の利用率が低い。特に反応温度が（触媒材料にも依るが）500℃以上の高温では後者の割合がかなり大きくなる。そこで、NO<sub>x</sub>を吸着触媒で排ガスから分離し（少なくとも排ガス中のO<sub>2</sub>から分離し）しかる後に還元剤と接触反

応させることによりNO<sub>x</sub>のN<sub>2</sub>への還元を効果的に行うことが可能となる。本発明では、NO<sub>x</sub>吸着触媒によりリーン排ガス中のNO<sub>x</sub>を吸着除去することにより排ガス中のNO<sub>x</sub>をO<sub>2</sub>から分離する。

【0016】本発明のNO<sub>x</sub>吸着触媒においては、次に、排ガス中の酸化剤（O<sub>2</sub>、NO<sub>x</sub>等）と還元剤（HC、CO、H<sub>2</sub>等）で構成される酸化還元系において還元剤が同量かもしくは卓越する状態をつくり、吸着触媒上に吸着したNO<sub>x</sub>をHC等の還元剤と接触反応させてN<sub>2</sub>に還元する。

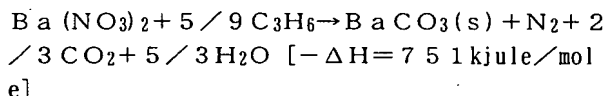
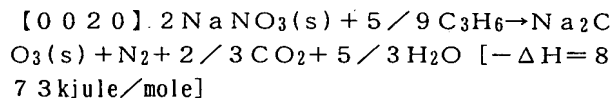
【0017】ところで排ガス中のNO<sub>x</sub>はほぼNOとNO<sub>2</sub>からなる。NO<sub>2</sub>はNOに比べて反応性に富む。したがってNO<sub>2</sub>の吸着除去と還元はNOよりも容易である。したがってNOをNO<sub>2</sub>に酸化すれば排ガス中のNO<sub>x</sub>の吸着除去と還元が容易となる。本発明はリーン排ガス中のNO<sub>x</sub>を共存するO<sub>2</sub>によりNO<sub>2</sub>に酸化し除去する方法、そのための酸化手段例えば吸着触媒にNO酸化機能を持たせたり吸着触媒前段に酸化触媒を設けることをも包含するものである。

【0018】本発明のNO<sub>x</sub>吸着触媒における、化学吸着したNO<sub>x</sub>の還元反応はおおよそ以下の反応式で記述できる。



ここに、Mは金属元素（還元生成物にMCO<sub>3</sub>を採用した理由は後述する）

上記の反応は発熱反応である。金属Mとしてアルカリ金属とアルカリ土類金属を取り上げ、それぞれNa及びBaを代表させて反応熱を評価すると標準状態（1気圧、25℃）では以下となる。



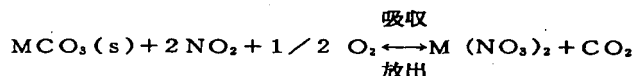
ここに、s：固体      g：気体

吸着種の熱力学量には相当する固体の値を用いた。

【0021】ちなみにC<sub>3</sub>H<sub>6</sub> 5/9moleの燃焼熱は107.0kJ/moleであり、上記各反応はHCの燃焼熱に匹敵する発熱量である。当然のことながらこの発熱は接触する排ガスに伝えられ吸着触媒表面の局所的な温度上昇は抑制される。

【0022】NO<sub>x</sub>の捕捉剤がNO<sub>x</sub>吸収剤の場合、吸収剤のバルク内に捕捉されたNO<sub>x</sub>も還元されるため発熱量は大きくなり、排ガスへの伝達には限度があるため吸収剤の温度上昇をもたらす。この発熱は下式に示す吸着反応の平衡を放出側にずらす。

## 【0023】



放出したNO<sub>x</sub>を速やかに還元して装置外へ排出される排ガス中のNO<sub>x</sub>濃度を低減すべく還元剤の濃度を高めても、気相においてはNO<sub>2</sub>とHCの反応はあまり進まない。したがって、還元剤の増量でNO<sub>x</sub>放出量を十分に減らすことができない。また、NO<sub>x</sub>吸収量が少ない段階で還元反応による操作を行うことも考えられるが、NO<sub>x</sub>吸収剤の再生頻度が増し、実用的でない。

【0024】本発明の吸着触媒は、その表面近傍でのみNO<sub>x</sub>を捕捉するため発熱の絶対量としては少なく、且つ速やかに排ガスに伝達されるため吸着触媒の温度上昇は少ない。したがって一旦捕捉したNO<sub>x</sub>の放出を防止することができる。

【0025】本発明のNO<sub>x</sub>吸着触媒は、NO<sub>x</sub>をその表面で化学吸着により捕捉しNO<sub>x</sub>の還元の際に際しての発熱反応でNO<sub>x</sub>の放出を生起しない材料として特徴付けられる。また、本発明のNO<sub>x</sub>吸着触媒は、NO<sub>x</sub>をその表面で化学吸着によりもしくは表面近傍で化学結合により捕捉し、NO<sub>x</sub>の還元の際に際しての発熱反応でNO<sub>x</sub>の放出を生起しない材料として特徴付けられる。

【0026】本発明者等は、少なくともカリウム(K)、ナトリウム(Na)、マグネシウム(Mg)、ストロンチウム(Sr)及びカルシウム(Ca)から選ばれる一種以上の元素を成分の一部として含むNO<sub>x</sub>吸着触媒で上記特徴を実現し得ることを見出した。

【0027】本発明の内燃機関の排ガス浄化装置は、少なくともカリウム(K)、ナトリウム(Na)、マグネシウム(Mg)、ストロンチウム(Sr)及びカルシウム(Ca)から選ばれる一種以上の元素を成分の一部として含むNO<sub>x</sub>吸着触媒を排ガス流路に配置し、排ガス中の各成分間の酸化還元化学量論関係において還元剤に対して酸化剤が多い状態をつくって吸着触媒上にNO<sub>x</sub>を化学吸着させ、次に酸化剤に対し還元剤が同量以上の状態をつくり、吸着触媒上に吸着したNO<sub>x</sub>を還元剤と接触反応させてN<sub>2</sub>に還元して無害化することを特徴とする。

【0028】本発明の内燃機関の排ガス浄化装置は、また、少なくともカリウム(K)、ナトリウム(Na)、マグネシウム(Mg)、ストロンチウム(Sr)及びカルシウム(Ca)から選ばれる一種以上の元素を成分の一部として含むNO<sub>x</sub>吸着触媒を排ガス流路に配置し、酸化還元化学量論関係においてHC等の還元剤に対してO<sub>2</sub>等の酸化剤が多い状態をつくって吸着触媒表面及び表面近傍にNO<sub>x</sub>を化学結合により捕捉し、次に酸化剤に対し還元剤が同量かもしくは多い状態をつくり、吸着触媒に捕捉されたNO<sub>x</sub>を還元剤と接触反応させてN<sub>2</sub>に還元して無害化することを特徴とする。

【0029】本発明におけるNO<sub>x</sub>吸着触媒としては特

に以下が好適に適用できる。

【0030】カリウム(K)、ナトリウム(Na)、マグネシウム(Mg)、ストロンチウム(Sr)及びカルシウム(Ca)から選ばれる少なくとも一種と、セリウム等からなる希土類から選ばれる少なくとも一種と、白金、ロジウム、パラチウム等からなる貴金属から選ばれる少なくとも一種の元素を含む、金属および金属酸化物(もしくは複合酸化物)からなる組成物、該組成物を多孔質耐熱性金属酸化物に担持してなる組成物。本組成物は、優れたNO<sub>x</sub>吸着能に加え優れた耐SO<sub>x</sub>性を有する。

【0031】本発明の方法における、酸化剤に対し還元剤が同量かもしくは多い状態は以下の方法で作る事ができる。

【0032】内燃機関における燃焼条件を理論空燃比もしくは燃料過剰(リッチ)とする。また、リーンバーン排ガスに還元剤を添加する。

【0033】前者は以下の方法で達成することができる。

【0034】排気ダクトに設けられた酸素濃度センサー出力及び吸気流量センサー出力等に応じて燃料噴射量を制御する方法。本法では、複数の気筒の一部を燃料過剰とし残部を燃料不足とし、全気筒からの混合排ガス中の成分が酸化還元化学量論関係において酸化剤に対して還元剤が同量かもしくは多い状態をつくる方法をも含む。

【0035】後者は以下の各方法で達成することができる。

【0036】排ガス流の吸着触媒上流に還元剤を投入する方法。還元剤には内燃機関の燃料としてのガソリン、軽油、灯油、天然ガス、これらの改質物、水素、アルコール類、アンモニア等が適用できる。

【0037】ブローバイガス及びキャニスターバージガスを吸着触媒上流に導きこれらに含まれる炭化水素等の還元剤を投入することも有効である。燃料直噴式内燃機関においては、排気行程で燃料を噴射し還元剤としての燃料を投入することが有効である。

【0038】本発明における、吸着触媒は、各種の形状で適用することができる。コージェライト、ステンレス等の金属材料からなるハニカム状構造体に吸着触媒成分をコーティングして得られるハニカム形状を始めとし、ペレット状、板状、粒状、粉末として適用できる。

【0039】本発明における、酸化剤に対し還元剤が同量かもしくは多い状態を作るタイミングは以下の各方法によることができる。

【0040】ECU(Engine Control Unit)で決定される空燃比設定信号、エンジン回転数信号、吸入空気量信号、吸気管圧力信号、速度信号、スロットル開度、排ガ

ス温度等からリーン運転時における $\text{NO}_x$ 排出量を推定し、その積算値が所定の設定値を超えたとき。

【0041】排気流路の吸着触媒上流または後流に置かれた酸素センサー（もしくはA/Fセンサー）の信号により累積酸素量を検出し累積酸素量が所定の量を超えたとき。その変形態様として、リーン運転時の累積酸素量が所定の量を超えたとき。

【0042】排気流路の吸着触媒上流に置かれた $\text{NO}_x$ センサー信号により累積 $\text{NO}_x$ 量を算出し、リーン運転時における累積 $\text{NO}_x$ 量が所定の量を超えたとき。

【0043】排気流路の吸着触媒後流に置かれた $\text{NO}_x$ センサーの信号によりリーン運転時における $\text{NO}_x$ 濃度を検出し、 $\text{NO}_x$ 濃度が所定濃度を超えたとき。

【0044】本発明における、酸化剤に対し還元剤が同量もしくは多い状態を維持する時間もしくは維持すべく投入する還元剤量は、前述のごとく、予め吸着触媒の特性、内燃機関の諸元と特性等を考慮して決めることができるが、これらは、燃料噴射弁のストローク、噴射時間及び噴射間隔を調整して実現できる。

【0045】

【発明の実施の形態】本発明の具体的実施態様を挙げて本発明を詳細に説明する。なお、本発明は以下の実施態様及び実施例に限定されるものでなく、その思想範囲内において各種の実施態様があることは言うまでもない。

【0046】〔吸着触媒〕本発明の方法による吸着触媒の特性について説明する。アルカリ金属としてNaを含むN-N9とKを含むN-K9の特性は次の様である。

《吸着触媒調製法》吸着触媒N-N9を以下の方法で得た。

【0047】アルミナ粉末とペーマイトを硝酸邂逅して得たバインダーとしてのアルミナゾルを混合し硝酸酸性アルミナスラリーを得た。該コーティング液にハニカムを浸漬した後速やかに引き上げ、セル内に閉塞した液をエアブローして除去した後、乾燥、続いて450℃で焼成した。この操作を繰返しハニカムの見掛け容積1Lあたり150gのアルミナをコーティングした。該アルミナコートハニカムに触媒活性成分担持しハニカム状吸着触媒を得た。例えば、硝酸セリウム（硝酸Ce）溶液を含浸し乾燥後600℃で1時間焼成した。続いて硝酸ナトリウム（硝酸Na）溶液とチタニアゾル溶液と硝酸マグネシウム（硝酸Mg）溶液の混合溶液を含浸し、同様に乾燥、焼成した。さらにジニトジアンミンPt硝酸溶液と硝酸ロジウム（硝酸Rh）溶液の混合溶液に含浸し、乾燥後450℃で1時間焼成した。最後に硝酸Mg溶液を含浸し450℃で1時間焼成した。以上によりアルミナ（ $\text{Al}_2\text{O}_3$ ）にCe、Mg、Na、Ti、Rh、Ptを担持したハニカム状吸着触媒、 $2\text{Mg}-(0.2\text{Rh}, 2.7\text{Pt})-(18\text{Na}, 4\text{Ti}, 2\text{Mg})-27\text{Ce}/\text{Al}_2\text{O}_3$ を得た。ここで、 $\text{Al}_2\text{O}_3$ は活性成分が $\text{Al}_2\text{O}_3$ 上に担持されたことを示し、元素記号前の数値はハ

ニカム見掛け容積1Lあたりに担持した表示金属成分の重量(g)である。表記順序は担持順序を示しており、 $\text{Al}_2\text{O}_3$ に近く表記される成分から離れる成分の順で担持し、( )で括られた成分は同時に担持した。ちなみに各活性成分の担持量は含浸溶液中の活性成分濃度を変化させることにより変えることができる。

【0048】吸着触媒N-K9を以下の方法で調製した。

【0049】吸着触媒N-N9調製における硝酸Na溶液に代わり硝酸カリウム（硝酸K）溶液を用い、その他は吸着触媒N-N9同様の方法でN-K9  $2\text{Mg}-(0.2\text{Rh}, 2.7\text{Pt})-(18\text{K}, 4\text{Ti}, 2\text{Mg})-27\text{Ce}/\text{Al}_2\text{O}_3$ を得た。また同様の方法で比較触媒N-R  $2\text{Mg}-(0.2\text{Rh}, 2.7\text{Pt})-27\text{Ce}/\text{Al}_2\text{O}_3$ を得た。

【0050】《性能評価法》上記方法で得た吸着触媒を700℃で5時間酸化雰囲気中で熱処理した後、以下の方法で特性を評価した。

【0051】排気量1.8Lのリーンバーン仕様ガソリンエンジンを搭載した乗用車に本発明の方法により調製した容積1.7Lのハニカム状吸着触媒を搭載し $\text{NO}_x$ 浄化特性を評価した。

【0052】《吸着触媒の特性》吸着触媒N-N9を搭載し、A/F=13.3のリッチ運転30秒間とA/F=22のリーン運転約20分間を交互に繰返し図2の $\text{NO}_x$ 浄化率経時特性を得た。同図から本吸着触媒によりリーン運転期間中の $\text{NO}_x$ が浄化されることが伺える。リーン運転中 $\text{NO}_x$ 浄化率は徐々に低下し初期に100%あった浄化率は20分後には約40%となる。しかしこの低下した浄化率は30秒間のリッチ運転で100%にまで回復する。再びリーン運転を行うと $\text{NO}_x$ 浄化率は回復して前述の経時変化を繰り返す。リーン運転とリッチ運転を複数回繰返してもリーン運転中の $\text{NO}_x$ 浄化率の経時低下の速度は不変であり、これはリッチ運転により $\text{NO}_x$ 吸着性能が十分に再生されたことを示している。

【0053】車速を約40km/h一定（排ガスの空間速度（SV）約20,000/h一定）とし点火時期を変化させて排ガス中の $\text{NO}_x$ 濃度を変え、 $\text{NO}_x$ 濃度とリーン排ガス中の $\text{NO}_x$ 浄化率の関係を求めて図3を得た。 $\text{NO}_x$ 浄化率は経時的に低下するが $\text{NO}_x$ 濃度が低いほど低下速度は小さい。 $\text{NO}_x$ 浄化率50%及び30%に至るまでに捕捉された $\text{NO}_x$ 量を同図から求めると表1となる。

【0054】 $\text{NO}_x$ 捕捉量は $\text{NO}_x$ 濃度に依らずほぼ一定である。吸着量が吸着質の濃度（圧力）に寄らないのは化学吸着の特徴である。

【0055】供試吸着触媒中で $\text{NO}_x$ 吸着剤として先ず考えられるのはPt粒子である。露出Pt量を評価する手段として多用されるCO吸着量評価を行ったところC

〇吸着量(a t 100℃)は $4.5 \times 10^{-4}$ molであった。この値は上記NO<sub>x</sub>吸着量の約1/100でありPtがNO<sub>x</sub>吸着剤の主役でないことは明らかである。

【0056】一方、本吸着触媒のコーゼライトごと測定したBET比表面積(窒素吸着で測定)は約25m<sup>2</sup>/gでハニカム1.7L当たり28,050m<sup>2</sup>であった。また、本発明の吸着触媒のNaの化学構造について検討したところ、鉍酸にCO<sub>2</sub>ガスを発生して溶解すること及び鉍酸による中和滴定曲線における変曲点の値から判断して主にNa<sub>2</sub>CO<sub>3</sub>として存在すると判断できた。仮に全ての表面がNa<sub>2</sub>CO<sub>3</sub>が占められているとすると表面には0.275molのNa<sub>2</sub>CO<sub>3</sub>が露出していることになる(Na<sub>2</sub>CO<sub>3</sub>の比重が2.533g/mlであることからNa<sub>2</sub>CO<sub>3</sub>1分子の体積が求まる(Na<sub>2</sub>CO<sub>3</sub>を立方体と仮定してその1面の面積を求めこれを表面Na<sub>2</sub>CO<sub>3</sub>の占有面積とした)。前出の反応式に従えば0.275molのNa<sub>2</sub>CO<sub>3</sub>は0.55molのNO<sub>2</sub>を吸着する能力がある。しかし、実際に本発明の吸着触媒が除去したNO<sub>x</sub>量はその1/10以下の0.04molのオーダーである。この相違はBET法が物理表面積を評価するものでAl<sub>2</sub>O<sub>3</sub>等のNa<sub>2</sub>CO<sub>3</sub>以外の表面積も評価していることによる。以上の評価は、吸着NO<sub>x</sub>量はNa<sub>2</sub>CO<sub>3</sub>バルクのNO<sub>x</sub>捕捉能よりはるかに少なく、少なくともNO<sub>x</sub>がNa<sub>2</sub>CO<sub>3</sub>表面が表面近傍に限られた領域で捕捉されていることを示している。

【0057】図3において前記NO<sub>x</sub>吸着能力は自動車の走行距離の増加に伴い、低下し、ストイキ運転からリーン運転に切り替えた後のNO<sub>x</sub>浄化率の減少速度が速くなる。これは排ガス中に含まれる被毒物(SO<sub>x</sub>等)がNO<sub>x</sub>吸着物質と反応し、吸着能力を低下させるためである。この劣化は内燃機関から排出される排気を理論空燃比もしくは燃料過剰(リッチ)の状態とし、排気温度を所定以上に所定期間以上保持することにより、経時的に蓄積された触媒の被毒物を触媒から排除することにより回復させることができる。

【0058】図4は、リーン運転からストイキ運転に切替えた直後のNO<sub>x</sub>浄化率を示す。本吸着触媒では、ストイキ運転への切替え直後から90%以上のNO<sub>x</sub>浄化率が得られることが分かる。

【0059】図5、図6に、リーンからストイキあるいはリッチへの切替え前後におけるNO<sub>x</sub>浄化特性を示した。図5は吸着触媒N-N9の入口と出口のNO<sub>x</sub>濃度を示したもので、図(a)はA/F=22のリーンからA/F=14.2のリッチへ空燃比を切替えた場合である。リッチ切替え直後の再生の開始時点においてはA/F=14.2の排ガスNO<sub>x</sub>濃度が高いためリッチ運転の入口NO<sub>x</sub>濃度が大きく増加し、これに伴い過渡的に出口NO<sub>x</sub>濃度は増加するが、常時出口NO<sub>x</sub>濃度は入口NO<sub>x</sub>濃度を大きく下回る。再生は速やかに進み短時間で出口NO<sub>x</sub>濃度は0近傍に到達する。図(b)はA/F

F=22のリーンからA/F=14.2のリッチへ空燃比を切替えた場合であるが、図(a)と同様に、常時出口NO<sub>x</sub>濃度は入口NO<sub>x</sub>濃度を大きく下回り、且つ、より短時間で出口NO<sub>x</sub>濃度は0近傍に到達する。

【0060】以上から明らかであるが、再生条件としてのA/F値は再生に要する時間に影響する。再生に適したA/F値、時間、さらには還元剤量は、吸着触媒の組成、形状、温度、SV値、還元剤の種類、排気流路の形状や長さの影響を受ける。従って、再生条件はこれらを考慮して総合的に決められるものである。

【0061】図6は吸着触媒N-K9の入口と出口のNO<sub>x</sub>濃度を示したもので、図(a)はA/F=22のリーンからA/F=14.2のリッチへ空燃比を切替えた場合、図(b)はA/F=22のリーンからA/F=14.2のリッチへ空燃比を切替えた場合であるが、上述の吸着触媒N-N9の場合と同様に常時出口NO<sub>x</sub>濃度は入口NO<sub>x</sub>濃度を大きく下回り、且つ、短時間で吸着触媒の再生が進んでいる。

【0062】[排気浄化制御装置]図1は本発明の排ガス浄化制御装置の一実施態様を示す装置の全体構成である。

【0063】本発明の装置は、リーンバーン可能なエンジン99、エアフローセンサー2、電子制御スロットルバルブ3等を擁する吸気系、酸素濃度センサー(or A/Fセンサー)19、排気温度センサー17、NO<sub>x</sub>吸着触媒18等を擁する排気系及び制御ユニット(ECU)等から構成される。ECUは入出力インターフェイスとしてのI/O LSI、演算処理装置MPU、多数の制御プログラムを記憶させた記憶装置RAMおよびROM、タイマーカウンタ等より構成される。以上の排気浄化制御装置は、以下のように機能する。エンジンへの吸入空気はエアクリーナー1により濾過された後エアフローセンサー2により計量され、電子制御スロットルバルブ3を経て、さらにインジェクター5から燃料噴射を受け、混合気としてエンジン99に供給される。エアフローセンサー信号その他のセンサー信号はECU(Engine Control Unit)へ入力される。

【0064】ECUでは後述の方法によって内燃機関の運転状態及びNO<sub>x</sub>吸着触媒の状態を評価して運転空燃比を決定し、インジェクター5の噴射時間等を制御して混合気の燃料濃度を所定値に設定する。また、電子制御スロットルバルブ3の開度調整で混合気の燃料濃度を所定値に設定してもよい。シリンダーに吸入された混合気はECU25からの信号で制御される点火プラグ10により着火され燃焼する。燃焼排ガスは排気浄化系に導かれる。排気浄化系にはNO<sub>x</sub>吸着触媒が設けられ、ストイキ運転時にはその三元触媒機能により排ガス中のNO<sub>x</sub>、HC、COを浄化し、また、リーン運転時にはNO<sub>x</sub>吸着能によりNO<sub>x</sub>を浄化すると同時に併せ持つ燃焼機能により、HC、COを浄化する。さらに、ECUの

判定及び制御信号により、リーン運転時には $\text{NO}_x$ 吸着触媒の $\text{NO}_x$ 浄化能力を常時判定して、 $\text{NO}_x$ 浄化能力が低下した場合燃焼の空燃比等をリッチ側にシフトして吸着触媒の $\text{NO}_x$ 吸着能を回復させる。以上の操作により、本装置では、リーン運転、ストイキ（含むリッチ）運転の全てのエンジン燃焼条件下における排ガスを効果的に浄化する。

【0065】エンジンに供給される混合気の燃料濃度（以下空燃比）は次の様に制御される。図7に空燃比制御方法をブロック線図で示した。

【0066】アクセルペダルの踏み込みに応じた信号を出力する負荷センサー出力、エアフローセンサーにより計量された吸気量の出力信号、クランク角センサーにより検出されるエンジン回転数信号、排ガス温度信号、スロットル開度を検出するスロットルセンサー信号、エンジン冷却水温信号、スターター信号等の情報からECU 25は空燃比（ $A/F$ ）を決定し、さらにこの信号は酸素センサーからフィードバックされる信号に基づき補正され、燃料噴射量を決定する。なお、低温時、アイドル時、高負荷時等では各センサー及びスイッチの信号によりフィードバック制御を停止する。また、空燃比補正学習機能により空燃比の微妙な変化や急な変化にも正確に対応できるよう空燃比補正学習機能で対応する。

【0067】決定された空燃比がストイキ（ $A/F=14.7$ ）及びリッチ（ $A/F<14.7$ ）のときECUの指示によりインジェクタの噴射条件が決定されストイキ及びリッチ運転が行われる。電子制御スロットルバルブ3の開度調整によりストイキおよびリッチ運転を行ってもよい。一方、リーン（ $A/F>14.7$ ）運転が決定された場合、 $\text{NO}_x$ 吸着触媒の $\text{NO}_x$ 吸着能の有無の判定を行い吸着能があると判定された場合に指示通りのリーン運転を行うべく燃料噴射量が決定され、吸着能がないと判定された場合には空燃比を所定期間リッチシフトして $\text{NO}_x$ 吸着触媒を再生する。リーン運転は電子制御スロットルバルブ3を開いて、吸入空気量を増加させることで行ってもよい。

【0068】前記 $\text{NO}_x$ 吸着触媒の再生処理に加え、所定の走行距離毎、または吸入空気量の積算値が所定量を越える毎に、排気温度が所定以上になるような運転条件で運転する。この処理を加えることにより被毒物質の蓄積により劣化した $\text{NO}_x$ 吸着能力を回復させることができる。排気温度を上昇させる手段としては、点火時期を遅らせる、電子制御スロットルバルブ3を開いて、吸入空気量を増加させる、排気管に2次空気を導入する、リーンからストイキに戻す、失火させて触媒の内部温度を上昇させる方法などがある。

【0069】図8（a）に前記の被毒時の回復処理のフローチャートを示した。

【0070】図8（b）に空燃比制御のフローチャートを示した。ステップ1002で各種の運転条件を指示す

るあるいは運転状態を検出する信号を読み込む。これらの信号に基づきステップ1003で空燃比を決定、ステップ1004では決定された空燃比を検出する。ステップ1005で決定された空燃比と理論空燃比との大きさを比較する。ここでの比較対象となる理論空燃比は、正確には吸着触媒において $\text{NO}_x$ の接触還元反応の速度が吸着による捕捉速度を上回る空燃比であり、予め吸着触媒の特性を評価して決定されるもので、理論空燃比近傍の空燃比が選定される。ここで、設定空燃比 $\leq$ 理論空燃比の場合ステップ1006に進み吸着触媒の再生操作を行うことなく指示通りの空燃比運転を行う。設定空燃比 $>$ 理論空燃比の場合ステップ1007に進む。ステップ1007では $\text{NO}_x$ 吸着量の推定演算を行う。推定演算方法については後述する。続いてステップ1008で推定 $\text{NO}_x$ 吸着量が所定限界量以下であるか否かを判定する。限界吸着量は予め実験等により吸着触媒の $\text{NO}_x$ 捕捉特性を評価して、また排ガス温度や吸着触媒温度等を考慮して、排ガス中の $\text{NO}_x$ が十分に浄化できる値に設定される。 $\text{NO}_x$ 吸着能がある場合にはステップ1006に進み、吸着触媒の再生操作を行うことなく指示通りの空燃比運転を行う。 $\text{NO}_x$ 吸着能がない場合にはステップ1009に進み、空燃比をリッチ側にシフトする。ステップ1010ではリッチシフト時間をカウントし、経過時間 $T_r$ が所定の時間（ $T_r$ ） $c$ を超えればリッチシフトを終了する。

【0071】 $\text{NO}_x$ 吸着能の判定は次のように行うことができる。

【0072】図9はリーン運転時の各種運転条件から $\text{NO}_x$ 排出量を積算し判定する方法である。

【0073】ステップ1007-E01で排ガス温度等の $\text{NO}_x$ 吸着触媒の作動条件に関する信号と排ガス中の $\text{NO}_x$ 濃度に影響する各種の機関運転条件に関する信号とを読み込み単位時間に吸着する $\text{NO}_x$ 量 $E_N$ を推算する。ステップ1007-E02で $E_N$ を積算し、ステップ1008-E01で積算値 $\Sigma E_N$ と吸着量の上限值（ $E_N$ ） $c$ との大きさを比較する。 $\Sigma E_N \leq (E_N) c$ の場合は積算を継続し、 $\Sigma E_N > (E_N) c$ の場合ステップ1008-E02で積算を解除しステップ1009に進む。

【0074】図10はリーン運転の積算時間で判定する方法である。

【0075】ステップ1007-H01でリーンの運転時間 $H_L$ を積算し、ステップ1008-H01で積算値 $\Sigma H_L$ と積算時間の上限值（ $H_L$ ） $c$ との大きさを比較する。 $\Sigma H_L \leq (H_L) c$ の場合積算を継続し、 $\Sigma H_L > (H_L) c$ の場合ステップ1008-H02で積算を解除しステップ1009に進む。

【0076】図11はリーン運転時の酸素センサー信号で判定する方法である。

【0077】ステップ1007-O01でリーン運転における酸素量 $Q_O$ を積算し、ステップ1008-O01



で積算値 $\Sigma Q_0$ と積算酸素量の上限值 $(Q_0)c$ との大小を比較する。 $\Sigma Q_0 \leq (Q_0)c$ の場合積算を継続し、 $\Sigma Q_0 > (Q_0)c$ の場合ステップ1008-002で積算を解除しステップ1009に進む。

【0078】図12はリーン運転時の $\text{NO}_x$ 吸着触媒入口で検出した $\text{NO}_x$ 濃度センサー信号で判定する方法である。

【0079】ステップ1007-N01で $\text{NO}_x$ 濃度センサー信号に基づき $\text{NO}_x$ 吸着触媒入口における $\text{NO}_x$ 量 $Q_N$ を積算する。ステップ1008-N01で積算値 $\Sigma Q_N$ と積算 $\text{NO}_x$ 量の上限值 $(Q_N)c$ との大小を比較する。 $\Sigma Q_N \leq (Q_N)c$ の場合積算を継続し、 $\Sigma Q_N > (Q_N)c$ の場合ステップ1008-N02で積算を解除しステップ1009に進む。

【0080】図13はリーン運転時の $\text{NO}_x$ 吸着触媒出口で検出した $\text{NO}_x$ 濃度センサー信号で判定する方法である。

【0081】ステップ1007-C01で $\text{NO}_x$ 濃度センサー信号に基づき $\text{NO}_x$ 吸着触媒入口における $\text{NO}_x$ 濃度 $C_N$ を検出する。ステップ1008-C01で $C_N$ と $C_N$ の上限值 $(C_N)c$ との大小を比較する。 $C_N \leq (C_N)c$ の場合検出を継続し、 $C_N > (C_N)c$ の場合ステップ1009に進む。

【0082】図14に本発明の排ガス浄化装置の他の実施態様を示す。図1の態様との相違は、エンジン近くの排気ダクトにマニホールド触媒17を設けた点にある。自動車排ガスの排出規制の強化は、エンジン起動直後に排出されるHC等の有害物の浄化を必要としている。すなわち従来は触媒が作動温度に達するまで未処理で排出されていたが、この量を大幅に低減する必要がある。これには、触媒を作動温度まで急速に昇温する方法が有効である。図14はエンジン起動時のHC、CO排出量低減と、リーン及びストイキ（含むリッチ）運転における排ガス浄化に対応できる装置構成である。図14の構成においてマニホールド触媒17にはPt、Rh、CeO<sub>2</sub>を主たる成分とするいわゆる三元触媒やこれらにPdを添加したりあるいはPd等の燃焼活性成分を中心成分とした燃焼触媒が適用できる。本構成では、起動時にはマニホールド触媒17が短時間で昇温してHCやCOの浄化を起動直後から行い、ストイキ運転時にはマニホールド触媒と吸着触媒18の双方が機能してHC、CO、 $\text{NO}_x$ の浄化を行い、リーン運転時は吸着触媒が $\text{NO}_x$ を吸着浄化する。吸着触媒の再生にあたり空燃比をリッチシフトすると還元剤としてのHC、COはマニホールド触媒で大きな化学変化を受けることなく吸着触媒に到達し、これを再生する。このような構成を可能とするの

は吸着触媒の大きな特徴である。

【0083】図15に本発明の排ガス浄化装置のさらに他の実施態様を示す。図1の態様との相違は、エンジン99が筒内噴射方式である点にある。本発明の装置は筒内噴射方式エンジンにも良好に適用することができる。

【0084】図16に本発明の排ガス浄化装置のさらに他の実施態様を示す。図1及び図15の態様との相違は、吸着触媒の下流に後触媒24を設けた点にある。たとえば後触媒に燃焼触媒を置くことによりHC浄化能を向上させた装置が、三元触媒を置くことによりストイキ時の三元機能を強化させた装置が、実現する。

【0085】図17に本発明の排ガス浄化装置のさらに他の実施態様を示す。図1及び図14～図16との相違は、リッチシフトの指示により、還元剤インジェクター23を通じて吸着触媒上流に燃料を添加することにある。本方式ではエンジンの運転状態を吸着触媒の状態と無関係に設定することができるという大きな利点がある。

【0086】図18に、本発明の方法による吸着触媒N-N9を搭載した場合、吸着触媒N-K9を搭載した場合、また比較の触媒N-R2を搭載した場合の、3度繰返される10モードの最後の10モードとそれに続く15モードにおける吸着触媒前後の $\text{NO}_x$ 濃度を示した。比較触媒は後掲の表2に示す組成のものとした。

【0087】図18において、吸着触媒N-N9およびN-K9を搭載した場合全運転域において出口 $\text{NO}_x$ 濃度は入口 $\text{NO}_x$ 濃度を下回り、リーン運転とストイキ運転が繰返されることにより吸着触媒が効果的に再生され $\text{NO}_x$ 浄化機能を保持し続けていることが分かる。一方、比較触媒N-R2においては出口 $\text{NO}_x$ 濃度が入口 $\text{NO}_x$ 濃度を上回る部分が生じている。

【0088】各種吸着触媒および比較触媒で得たCVS値を吸着触媒組成とともに表2及び表3に示した。吸着触媒および比較触媒の調製は前述の方法によったが、調製原料として、バリウム(Ba)には硝酸Baを、シリコン(Si)にはシリカゾルを用いた。Siはシリカ(SiO<sub>2</sub>)もしくはその複合酸化物として存在すると推定される。

【0089】以上から明らかな様に、本発明の装置によれば、排ガス流路に $\text{NO}_x$ 吸着触媒を設け、リーン排ガスの酸化雰囲気中で $\text{NO}_x$ を吸着捕捉し還元雰囲気をつくって吸着触媒を再生することにより、リーンバーン排ガス中の $\text{NO}_x$ 等を、燃費に大きな影響を与えることなく高効率で浄化できる。

【0090】

【表1】

表 1

入口排ガス中 NOx濃度(ppm)	浄化率50%になるまでに 浄化したNOx量 (mol)	浄化率30%になるまでに 浄化したNOx量 (mol)
約 50ppm	0.030	0.041
約120ppm	0.031	0.047
約230ppm	0.030	0.045
約450ppm	0.030	0.042
約550ppm	0.026	0.038

【0091】

【表2】

表 2

	記 号	組 成	CVS値(g/km)		
			NOx	HC	CO
比較 触媒	N-R1	(0.2Rh, 2.7Pt) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.18	0.02	0.07
	N-R2	2Mg - (0.2Rh, 2.7Pt) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.15	0.02	0.04
吸着 触媒	N-S1	2Mg - (0.2Rh, 2.7Pt) - 30Sr - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.08	0.10	0.08
	N-S2	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.09	0.08	0.08
	N-S3	(0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.11	0.08	0.11
	N-S4	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.10	0.07	0.09
	N-S5	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.10	0.08	0.09
	N-N1	2Mg - (0.2Rh, 2.7Pt) - 18Na - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.03
	N-N2	2Mg - (0.2Rh, 2.7Pt) - (18Na, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.12	0.04
	N-N3	(0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.07	0.16	0.10
	N-N4	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.15	0.08
	N-N5	(0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.08	0.10	0.12
	N-N6	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.06
	N-N7	2Mg - (0.2Rh, 2.7Pt) - (10Na, 10Sr) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.05
	N-N8	(0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.07	0.12	0.07
	N-N9	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.04	0.11	0.04
	N-N10	2Mg - (0.2Rh, 2.7Pt) - (10Na, 10Sr, 2Mg) - 27Ce/Al <sub>2</sub> O <sub>3</sub>	0.04	0.06	0.04

【0092】

【表3】

表 3

	記 号	組 成	CVS値(g/km)		
			NOx	HC	CO
吸着触媒	N-K1	2Mg-(0.2Rh, 2.7Pt)-18K-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.03
	N-K2	2Mg-(0.2Rh, 2.7Pt)-(18K, 2Mg)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.05
	N-K3	(0.2Rh, 2.7Pt)-(18K, 4Ti)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.08	0.11	0.06
	N-K4	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Ti)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.08	0.05
	N-K5	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Si)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.05
	N-K6	(0.2Rh, 2.7Pt)-(18K, 10Sr)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.07	0.12	0.06
	N-K7	2Mg-(0.2Rh, 2.7Pt)-(18K, 10Sr)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.05
	N-K8	(0.2Rh, 2.7Pt)-(18K, 4Ti, 2Mg)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.10	0.07
	N-K9	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Ti, 2Mg)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.07	0.04
	N-K10	2Mg-(0.2Rh, 2.7Pt)-(10K, 10Sr, 2Mg)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.04	0.07	0.06
	N-M1	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 4Ti)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.05	0.08
	N-M2	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 10Si)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.08
	N-M3	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 10Sr)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.06	0.10	0.05
	N-M4	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 4Ti, 2Mg)-27Ce/Al <sub>2</sub> O <sub>3</sub>	0.05	0.11	0.05

【0093】

【発明の効果】本発明によれば、NO<sub>x</sub>吸着触媒が燃料に含まれる硫黄分等で被毒し、吸着性能が劣化しても所定の走行距離毎、または、吸入空気量の積算値が所定値を越える毎に排気温度が所定値の運転条件で運転されるので、被毒物質の蓄積が解消されて劣化したNO<sub>x</sub>吸着能力を回復させることができる。その結果、耐被毒性が向上され、長い間、NO<sub>x</sub>を高効率で浄化できる。

【図面の簡単な説明】

【図1】本発明の代表的な実施態様を示す本発明の方法による排ガス浄化装置の構成図。

【図2】本発明の方法によりリッチ運転とリーン運転を交互に繰返したときのNO<sub>x</sub>浄化率の経時特性。

【図3】走行距離とNO<sub>x</sub>浄化率の関係。

【図4】ストイキ排ガス中のNO<sub>x</sub>浄化率。

【図5】リッチ（ストイキ）運転からリーン運転に切替えたときの吸着触媒入口NO<sub>x</sub>濃度と出口NO<sub>x</sub>濃度の関係。

【図6】リッチ（ストイキ）運転からリーン運転に切替えたときの吸着触媒入口NO<sub>x</sub>濃度と出口NO<sub>x</sub>濃度の関係。

【図7】空燃比の制御方法を示すブロック線図。

【図8】（a）は空燃比の制御方法を示すフローチャート。（b）は空燃比の制御方法を示すフローチャート。

【図9】リーン運転時のNO<sub>x</sub>排出量積算判定方法を示すフローチャート。

【図10】図8のフローチャートにおけるNO<sub>x</sub>量推算部分。

【図11】図8のフローチャートにおけるNO<sub>x</sub>量推算部分。

【図12】図8のフローチャートにおけるNO<sub>x</sub>量推算部分。

【図13】図8のフローチャートにおけるNO<sub>x</sub>量推算部分。

【図14】マニホールド触媒を設けた実施態様を示す装置の構成図。

【図15】筒内噴射エンジンにおける実施態様を示す装置の構成図。

【図16】後触媒を設けた実施態様を示す装置の構成図。

【図17】吸着触媒の上流に還元剤を添加する実施態様を示す装置構成図。

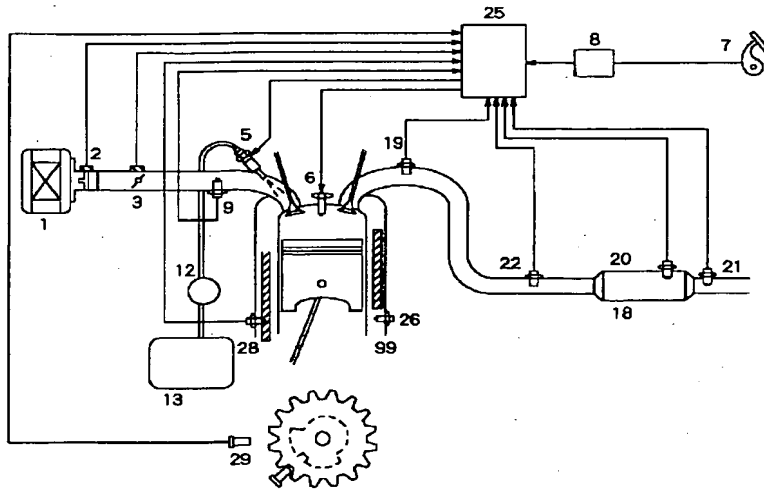
【図18】モード運転したときのNO<sub>x</sub>浄化特性図。

【符号の説明】

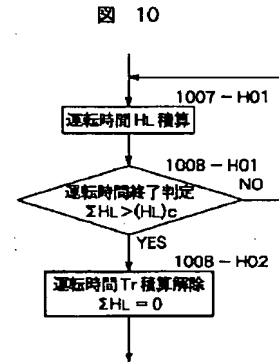
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一、20…吸着触媒温度センサー、21…排ガス温度センサー、22…NO<sub>x</sub>濃度センサー、23…還元剤インジェクター、24…後触媒、25…ECU、26…ソックセンサー、28…水温センサー、29…クランク角センサー、99…エンジン。

【図1】

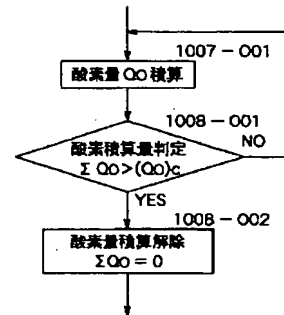


【図10】



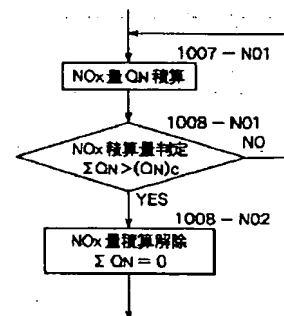
【図11】

図 11



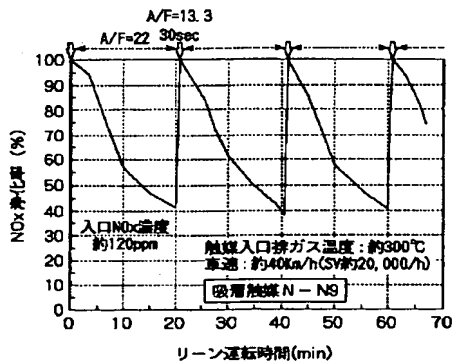
【図12】

図 12



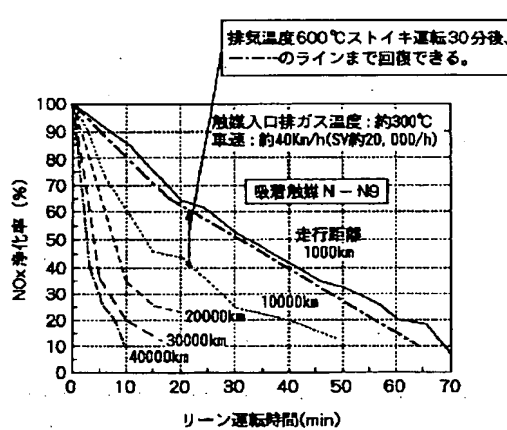
【図2】

図 2



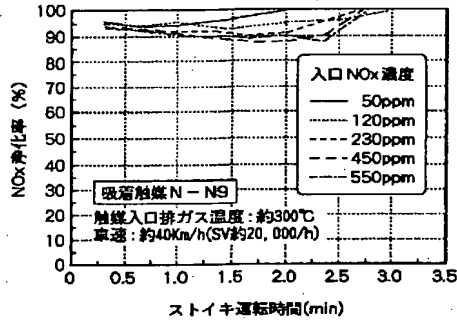
【図3】

図 3



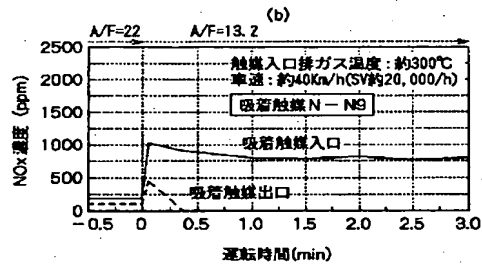
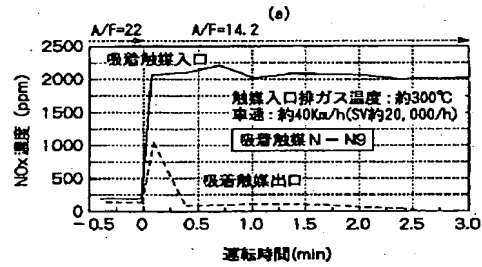
【図4】

図 4



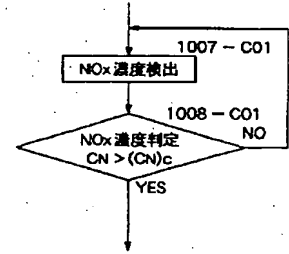
【図5】

図 5



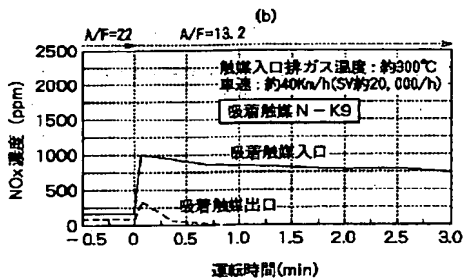
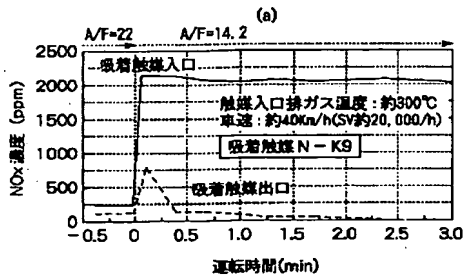
【図13】

図 13



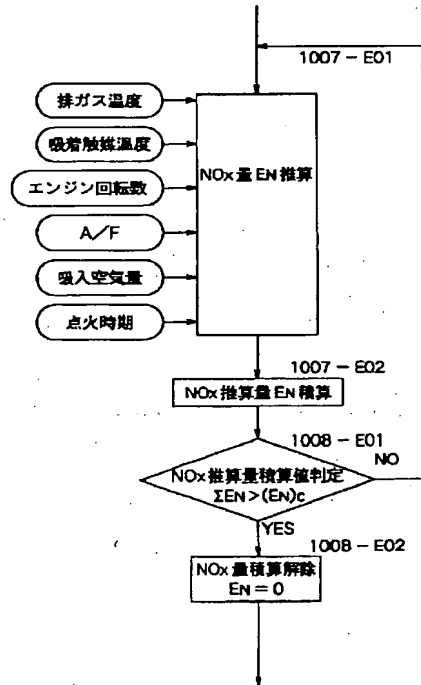
【図6】

図 6

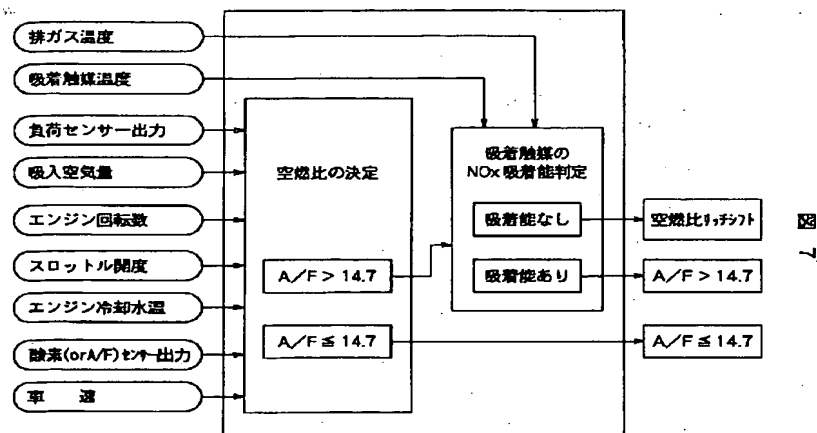


【図9】

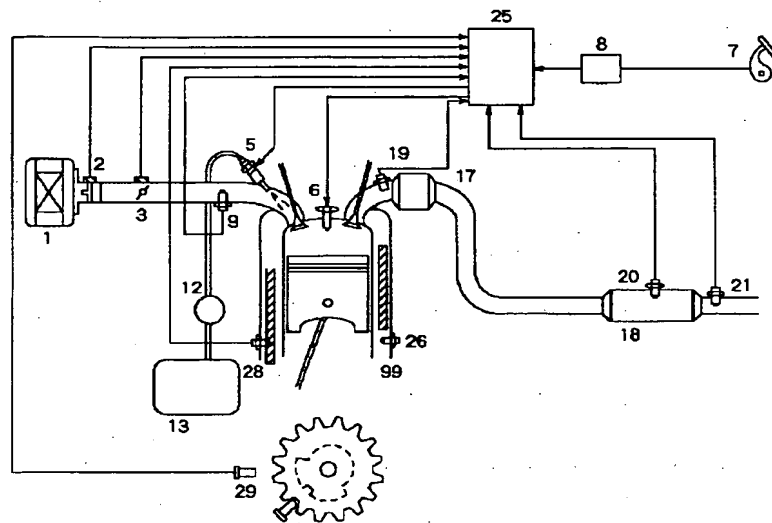
図 9



【図7】

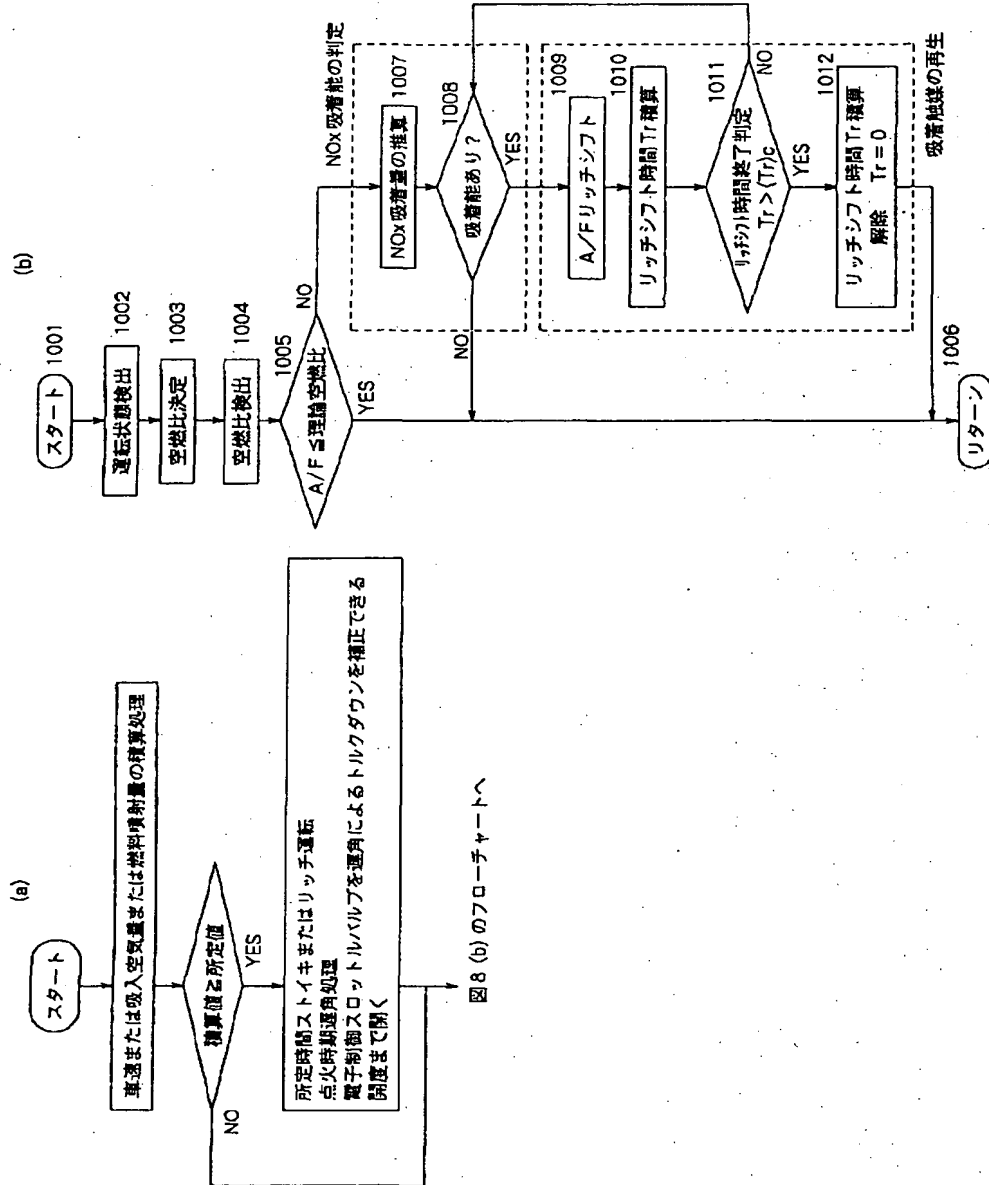


【図14】



【図 8】

図 8



【図 15】

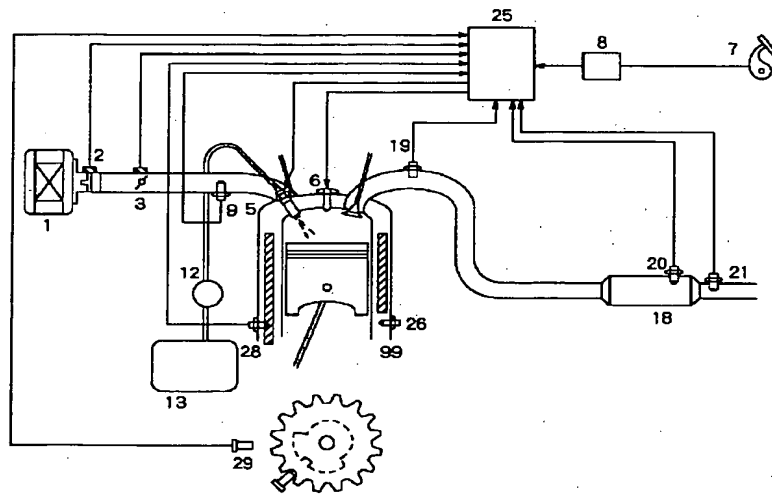


図 15

【図 16】

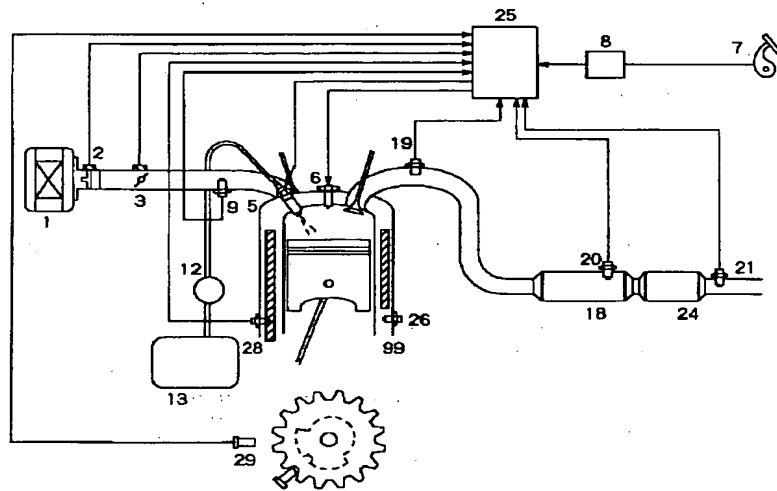


図 16





3/24 ZAB  
 3/28 ZAB  
 301  
 F02D 41/04 305  
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301C  
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 45/00 ZAB  
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 101Z

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**(54) EXHAUST EMISSION CONTROL DEVICE**

**(57) Abstract:**

**PROBLEM TO BE SOLVED:** To remove a positioning substance of a catalyst accumulated in the lapse of time from the catalyst by making exhaust gas exhausted from an internal combustion engine in a logical air-fuel ratio or rich fuel state and holding exhaust gas temperature at higher than specified for longer than a specified period of time.

**SOLUTION:** An ECU 25 decides an operating air fuel ratio by evaluating an operating state and a state of a NOx adsorptive catalyst 18 and sets fuel concentration at a specified value by controlling injection time of an injector 5, to. Air-fuel mixture is ignited and burnt by an ignition plug 6, and combustion exhaust gas is led

to an exhaust gas purifying system provided with the NOx adsorptive catalyst 18. At the time of stoichiometrical driving, NOx, NH, CO in exhaust gas is purified by its catalytic converter rhodium function, and at the time of lean driving, NOx is purified by a NOx adsorptive function and HC, CO is purified by a combustion function. Additionally, NOx purifying capacity of the NOx adsorptive catalyst 18 is constantly judged at the time of lean driving by judgement and a control signal of the ECU 25, and the NOx adsorptive capacity is recovered by shifting an air-fuel ratio of combustion, etc., to the rich side and holding exhaust gas temperature higher than specified and for longer than specified time.

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## CLAIMS

## [Claim(s)]

[Claim 1] In the oxidation reduction stoichiometry relation between each component in exhaust gas, NO<sub>x</sub> is chemisorbed in the state with many oxidizers to a reducing agent. The NO<sub>x</sub> adsorption catalyst which carries out catalytic reduction of the NO<sub>x</sub> to which the reducing agent stuck in the state more than the amount of said to the oxidizer is arranged to exhaust gas passage. In the oxidation reduction stoichiometry relation between each component in exhaust gas, build a state with many oxidizers to a reducing agent, and NO<sub>x</sub> is made to chemisorb on an adsorption catalyst. Next, to an oxidizer, a reducing agent builds the state more than the amount of said, catalytic reaction of the NO<sub>x</sub> which adsorbed on the adsorption catalyst is carried out to a reducing agent, and it is N<sub>2</sub>. In the exhaust gas purge of an internal combustion engine returned and made harmless The exhaust air purification control unit characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[Claim 2] At least A potassium (K), sodium (Na), magnesium (Mg), The NO<sub>x</sub> adsorption catalyst which contains the element more than a kind chosen from strontium (Sr) and calcium (calcium) as a part of component is arranged to exhaust gas passage. In the oxidation reduction stoichiometry relation between each component in exhaust gas, build a state with many oxidizers to a reducing agent, and NO<sub>x</sub> is made to chemisorb on an adsorption catalyst. Next, to an oxidizer, a reducing agent builds the state more than the amount of said, catalytic reaction of the NO<sub>x</sub> which adsorbed on the adsorption catalyst is carried out to a reducing agent, and it is N<sub>2</sub>. In the exhaust gas purge of an internal combustion engine returned and made harmless The exhaust air purification control unit characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[Claim 3] At least A potassium (K), sodium (Na), magnesium (Mg), The NO<sub>x</sub> adsorption catalyst which contains the element more than a kind chosen from strontium (Sr) and calcium (calcium) as a part of component is arranged to exhaust gas passage. a oxidation reduction stoichiometry relation -- setting -- reducing agents, such as HC, -- receiving -- O<sub>2</sub> Build a state with many oxidizers and NO<sub>x</sub> is caught by the chemical bond near an adsorption catalyst front face and the front face. etc. -- next, an oxidizer -- receiving -- a reducing agent -- the amount of said -- or many states are built and catalytic reaction of the NO<sub>x</sub> caught by the adsorption catalyst is carried out to a reducing agent -- making -- N<sub>2</sub> In the exhaust gas purge of an internal combustion engine returned and made harmless The exhaust air purification control unit characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[Claim 4] The claims 1 and 2 characterized by providing the following. It is to be chosen out of the rare

earth which is chosen from a potassium (K), sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium) and which consists of a kind, a cerium, etc. at least a kind that it is few. At least a kind of element chosen from the noble metals which consist of platinum, a rhodium, palladium, etc.

[Claim 5] It is to be chosen out of a potassium (K), sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium) in claims 1 and 2 a kind that it is few. It is to be chosen out of the rare earth which consists of a cerium etc. a kind that it is few. It is to be chosen out of the noble metals which consist of platinum, a rhodium, palladium, etc. a kind that it is few. The metal and metallic oxide (or multiple oxide) which contain at least a kind of element chosen from titanium and silicon It is the exhaust air purification control unit equipped with the above, and is characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[Claim 6] The exhaust air purification control unit characterized by controlling by the controlled variable of the air content inhaled by the internal combustion engine in claims 1-5 by relation in which the driving shaft torque of an automobile or the output torque of an internal combustion engine is not changed, fuel quantity, ignition timing, fuel injection timing, the change gear ratio of a change gear, and one combination of the engine speeds.

[Claim 7] The exhaust emission control device characterized by carrying out processing which eliminates the poisoning object of a catalyst from a catalyst by whether it is \*\*\*\*\* in claims 1-5 whenever the integrated value of every predetermined mileage of every predetermined period and an automobile, an inhalation air content, the amount of fuel supply, or displacement reaches a predetermined value.

[Claim 8] The exhaust emission control device characterized by carrying out when the degree of degradation of the NOx adsorption capacity force exceeds the processing which eliminates the poisoning object of a catalyst from a catalyst beyond a predetermined value in claims 1-5.

[Claim 9] The exhaust air purification control unit characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by increasing the quantity of the fuel supplied to an internal combustion engine in claims 1-5, making exhaust air into the state of theoretical air fuel ratio or overfuel (rich) by introducing air into an exhaust pipe, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[Claim 10] The exhaust air purification control unit characterized by eliminating from a catalyst the poisoning object of the catalyst accumulated with time in the claim 9 by [ which combine angle-of-delay control of ignition timing ] being alike and holding an exhaust-gas temperature more than a predetermined period more more than predetermined.

[Claim 11] The exhaust emission control device characterized by carrying out processing which eliminates the poisoning object of a catalyst from a catalyst by whether it is \*\*\*\*\* in claims 9-10 whenever the integrated value of every predetermined mileage of every predetermined period and an automobile, an inhalation air content, the amount of fuel supply, or displacement reaches a predetermined value.

[Claim 12] The exhaust emission control device characterized by carrying out when the degree of degradation of the NOx adsorption capacity force exceeds the processing which eliminates the poisoning object of a catalyst from a catalyst beyond a predetermined value in claims 9-10.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the purge of the exhaust gas discharged from the automobile carrying the internal combustion engine and this internal combustion engine which can be especially operated with a thin air-fuel ratio (RIN barn) with respect to the equipment which purifies the exhaust gas discharged from internal combustion engines, such as an automobile.

[0002]

[Description of the Prior Art] The carbon monoxide (CO) and hydrocarbon (HC:Hydrocarbon) which are contained in the exhaust gas discharged from internal combustion engines, such as an automobile, nitrogen oxide (NOx), etc. have a bad influence on a human body as an air pollution substance, and also occur problems, such as barring growth of vegetation. Then, from before, great efforts were paid to these discharge reduction, in addition to reduction of the yield by the improvement of the combustion method of an internal combustion engine, development of the method of purifying the discharged exhaust gas using a catalyst etc. was furthered, and the steady result has been mentioned. a gasoline engine vehicle -- being related -- a three way component catalyst -- the method using the catalyst which makes Pt and Rh the principal component of activity, performs oxidization of HC and CO and reduction of NOx simultaneously, and makes them harmless is in use

[0003] By the way, a three way component catalyst acts only on the exhaust gas which was burned near the theoretical air fuel ratio called a window, and was generated from the property effectively. Then, although an air-fuel ratio is conventionally changed according to an automobilism situation, the change range has been adjusted in principle near the theoretical air fuel ratio (in the case of a gasoline, on below  $A(\text{weight of air})/F(\text{weight of fuel}) = \text{abbreviation } 14.7$ ; book specifications, although a theoretical \*\*\*\* ratio is represented with  $A/F=14.7$ , this numeric value changes with a fuel seed.). However, if an engine can be operated with an air-fuel ratio thinner (RIN) than theoretical air fuel ratio, since mpg can be raised, the automobile which development of a RIN barn combustion technology is furthered

[ automobile ] and burns an internal combustion engine recently in a with an air-fuel ratios of 18 or more RIN region is not new. however -- above -- present -- business -- if RIN barn exhaust air is made to purify by the three way component catalyst, although oxidization purification of HC and CO can be performed, reduction purification of the NOx cannot be carried out effectively therefore, application to the large-size car of a RIN barn method and expansion (expansion of the application operation region of a RIN barn method) of a RIN barn burning time are advanced -- being alike -- RIN barn correspondence exhaust gas purification technology is needed Then, development of RIN barn correspondence exhaust air purification technology, i.e., the technology which purifies HC, NO, and NOx in the exhaust gas in which oxygen (O2) is contained so much, especially development of the technology which purifies NOx are furthered energetically.

[0004] In JP,63-61708,A, HC is supplied to the upstream of RIN barn exhaust gas, and it is O2 in exhaust gas. The method of lowering concentration to the concentration region where a catalyst

functions effectively, and pulling out the capacity of a catalyst is proposed.

[0005] JP,62-97630,A, No. 106826 [ 62 to ], and No. 117620 [ 62 to ] contact NO<sub>x</sub> in exhaust gas for the catalyst which has NO<sub>x</sub> (after changing into NO<sub>2</sub> which NO oxidizes and is easy to be absorbed) absorbing power, and carries out absorption removal. When an absorption efficiency falls, reduction removal of the NO<sub>x</sub> which stopped passage of exhaust gas and was accumulated using reducing agents, such as HC, such as H<sub>2</sub> and a methane gasoline, is carried out, and the method of reproducing the NO<sub>x</sub> absorbing power of a catalyst is shown.

[0006] Moreover, O<sub>2</sub> in the exhaust gas which flows into a NO<sub>x</sub> absorbent NO<sub>x</sub> which installed in the flueway the NO<sub>x</sub> absorbent which emits NO<sub>x</sub> absorbed when exhaust gas was RIN, NO<sub>x</sub> is absorbed to PCT/JP 92/01279 and PCT/JP 92/01330 and the oxygen density in exhaust gas was reduced to them, was made to absorb NO<sub>x</sub> when exhaust gas was RIN, and was made to absorb The exhaust emission control device to which concentration is made to fall to and is made to emit is proposed.

[0007] However, a lot of HC is needed for attaining composition (about about 0.5% of O<sub>2</sub> concentration) of the exhaust gas equivalent to about [ which is the air-fuel ratio as which a catalyst functions in JP,63-61708,A (A/F) ] 14.7. Although use of the blow-by gas of this invention is effective, it is not sufficient amount to process the exhaust gas under internal combustion engine operation. Although it is not technically impossible to throw in fuel, either, a result to which the mpg reduced by the RIN barn method is reduced is brought.

[0008] Moreover, in order to stop circulation of exhaust gas in reproduction of a NO<sub>x</sub> absorbent and to contact reducing agents, such as HC, to a NO<sub>x</sub> absorbent in JP,62-97630,A, 62-106826, and No. 117620 [ 62 to ], it is O<sub>2</sub> in the exhaust gas of a reducing agent. The combustion consumption to depend is suppressed sharply and the amount of the reducing agent used decreases sharply. However, the exhaust air change mechanism for preparing two NO<sub>x</sub> absorbents and circulating exhaust gas by turns to these is required, and structure of an exhaust air processor cannot deny a bird clapper intricately.

[0009] Furthermore, always circulate exhaust gas to a NO<sub>x</sub> absorbent, when exhaust gas is RIN, NO<sub>x</sub> is made to absorb in PCT/JP 92/01279 and PCT/JP 92/01330, and it is O<sub>2</sub> in exhaust gas. In order to make NO<sub>x</sub> which concentration was reduced and absorbed it emit and to reproduce an absorbent, the change of an emission is unnecessary and the trouble of the above-mentioned method is canceled. However, when sulfur (SO<sub>x</sub>) was contained in exhaust air, the NO<sub>x</sub> absorbent combined the above catalyst with SO<sub>x</sub>, and it became a sulfide, and it had the problem that absorptance was quickly inferior.

[0010]

[Problem(s) to be Solved by the Invention] In view of the trouble of the above-mentioned conventional technology, this invention is simple for the structure of an exhaust air processor, has little consumption of a reducing agent, and is to offer the exhaust air purification control unit excellent in endurance which can carry out [ removal and harmless ]-izing of the injurious ingredients, such as NO<sub>x</sub>, effectively from the RIN barn exhaust gas of an internal combustion engine.

[0011]

[Means for Solving the Problem] By making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined, the above-mentioned technical problem can recover the NO<sub>x</sub> adsorption capacity force in which it deteriorated by eliminating from a catalyst the poisoning object (SO<sub>x</sub>) of the catalyst accumulated with time, and can be solved. Although the NO<sub>x</sub> adsorption about a NO<sub>x</sub> adsorption catalyst and the reduction method are explained below, this NO<sub>x</sub> adsorption capacity force is inferior in connection with the accumulated dose to the catalyst of the sulfur content (SO<sub>x</sub>) contained in exhaust air.

[0012] In the NO<sub>x</sub> adsorption catalyst used for this invention, NO<sub>x</sub> is chemisorbed in the state with many oxidizers to a reducing agent in the oxidation reduction stoichiometry relation between each component in exhaust gas. The NO<sub>x</sub> adsorption catalyst which carries out catalytic reduction of the NO<sub>x</sub> to which the reducing agent stuck in the state more than the amount of said to the oxidizer is arranged to exhaust gas passage. In the oxidation reduction stoichiometry relation between each component in exhaust gas, build a state with many oxidizers to a reducing agent, and NO<sub>x</sub> is made to chemisorb on an



adsorption catalyst. Next, to an oxidizer, a reducing agent builds the state more than the amount of said, catalytic reaction of the NO<sub>x</sub> which adsorbed on the adsorption catalyst is carried out to a reducing agent, and it is N<sub>2</sub>. It is returned and made harmless.

[0013] An adsorption catalyst points out the material which has a catalyst function simultaneously with the capacity to adsorb matter, such as NO<sub>x</sub>, here. In this invention, material with the capacity which oxidizes in contact the capacity which adsorbs NO<sub>x</sub> and catches it, the capacity to return NO<sub>x</sub> in contact, HC, CO, etc. is pointed out.

[0014] moreover, an oxidizer -- O<sub>2</sub>, NO, and NO<sub>2</sub> etc. -- it is mainly oxygen as HC by which the internal combustion engine was presented with the reducing agent, and its derivative which generates by combustion assumption -- HC (included oxygenated hydrocarbon), CO, and H<sub>2</sub> etc. -- they are reducing matter, such as HC added in exhaust gas as the further below-mentioned reduction component

[0015] HC, CO, and H<sub>2</sub> as a reducing agent for returning RIN exhaust gas and NO<sub>x</sub> even to nitrogen etc. -- if it is made to contact -- these -- O<sub>2</sub> as an oxidizer in exhaust gas A combustion reaction is started. [ as mentioned above, ] NO<sub>x</sub> (NO and NO<sub>2</sub>) also reacts with these, and is returned to nitrogen. Usually, since both reactions are parallel and advance, under coexistence of oxygen, the utilization factor of a reducing agent is a low. Especially reaction temperature becomes [ the latter rate ] quite large at the elevated temperature of 500 (it depends also on catalyst material) degrees C or more. Then, it is N<sub>2</sub> of NO<sub>x</sub> by separating NO<sub>x</sub> from exhaust gas with an adsorption catalyst, and making after an appropriate time (dissociating from O<sub>2</sub> in exhaust gas at least) carry out catalytic reaction to a reducing agent. It becomes possible to return effectively. It is NO<sub>x</sub> in exhaust gas by carrying out the adsorption treatment of the NO<sub>x</sub> in RIN exhaust gas according to a NO<sub>x</sub> adsorption catalyst in this invention O<sub>2</sub> Shell separation is carried out.

[0016] the redox system which consists of [ in / the NO<sub>x</sub> adsorption catalyst of this invention / next ] the oxidizers (O<sub>2</sub>, NO<sub>x</sub>, etc.) and reducing agents in exhaust gas (HC, CO, H<sub>2</sub>, etc.) -- setting -- a reducing agent -- the amount of said -- or the state of standing high is built and catalytic reaction of the NO<sub>x</sub> which adsorbed on the adsorption catalyst is carried out to reducing agents, such as HC, -- making -- N<sub>2</sub> It returns.

[0017] by the way, NO<sub>x</sub> in exhaust gas -- almost -- NO and NO<sub>2</sub> from -- it becomes NO<sub>2</sub> Compared with NO, it is rich in reactivity. Therefore, NO<sub>2</sub> An adsorption treatment and reduction are easier than NO. Therefore, it is NO NO<sub>2</sub> If it oxidizes, the adsorption treatment of NO<sub>x</sub> in exhaust gas and reduction will become easy. this invention is O<sub>2</sub> which lives NO<sub>x</sub> in RIN exhaust gas together. NO<sub>2</sub> NO oxidization function is given to the method of oxidized and removing, and the oxidization means for it, for example, an adsorption catalyst, or it also includes preparing an oxidation catalyst in the adsorption catalyst preceding paragraph.

[0018] The following reaction formulae can describe about the reduction reaction of chemisorbed NO<sub>x</sub> in the NO<sub>x</sub> adsorption catalyst of this invention.

[0019]  $M\text{-NO}_3 + \text{HC} \rightarrow \text{MO} + \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{MCO}_3 + \text{N}_2 + \text{H}_2\text{O}$  -- here -- M -- a metallic element (the reason for having adopted MCO<sub>3</sub> as the reduction product is mentioned later)

The above-mentioned reaction is exothermic reaction. Alkali metal and alkaline earth metal are taken up as a metal M, and if Na and Ba are represented, respectively and heat of reaction is evaluated, in reference condition (one atmospheric pressure, 25 degrees C), it will become the following.

[0020]  $2\text{NaNO}_3(\text{s}) + 5/9\text{C}_3\text{H}_6 \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{N}_2 + 2/3\text{CO}_2 + 5/3\text{H}_2\text{O}$  [-deltaH=873 kjule/mole]

$\text{Ba}(\text{NO}_3)_2 + 5/9\text{C}_3\text{H}_6 \rightarrow \text{BaCO}_3(\text{s}) + \text{N}_2 + 2/3\text{CO}_2 + 5/3\text{H}_2\text{O}$  [-deltaH=751 kjule/mole]

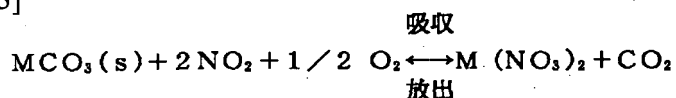
It is s:solid-state here. g: The value of a corresponding solid-state was used for the amount of thermodynamics of a gas-adsorption kind.

[0021] Incidentally they are C<sub>3</sub>H<sub>6</sub>/9mole. Heat of combustion is 1070kjule(s) and each above-mentioned reaction is calorific value which is equal to the heat of combustion of HC. It is told to the exhaust gas which this generation of heat contacts with a natural thing, and the local temperature rise of an adsorption catalyst front face is suppressed.

[0022] Since NO<sub>x</sub> caught in bulk of an absorbent is also returned when the scavenger of NO<sub>x</sub> is a NO<sub>x</sub> absorbent, calorific value becomes large, and since there is a limit in the transfer to exhaust gas, the

temperature rise of an absorbent is brought about. This generation of heat is shifted to a discharge-the balance of absorption reaction shown in lower formula side.

[0023]



Even if it raises the concentration of a reducing agent that the NOx concentration in the exhaust gas which returns emitted NOx promptly and is discharged out of equipment should be reduced, it sets to a gaseous phase, and it is NO2. The reaction of HC seldom progresses. Therefore, a NOx burst size is fully unreducible by increase in quantity of a reducing agent. Moreover, although performing operation by the reduction reaction in a stage with few amounts of NOx absorption is also considered, the reproduction frequency of a NOx absorbent increases and it is not practical.

[0024] Since it is transmitted to exhaust gas that it is few and promptly as absolute magnitude of generation of heat in order that the adsorption catalyst of this invention may catch NOx only near [ the ] the front face, there are few temperature rises of an adsorption catalyst. Therefore, discharge of once caught NOx can be prevented.

[0025] Discharge of NOx is characterized as a material not occurring by the NOx adsorption catalyst of this invention by the exothermic reaction for [ catches NOx by chemical absorption on the front face, and ] reduction of NOx. moreover, the NOx adsorption catalyst of this invention -- NOx -- the front face -- chemical absorption -- or it catches by the chemical bond near the front face, and discharge of NOx is characterized by the exothermic reaction for reduction of NOx as a material not occurring

[0026] this invention person etc. found out that the above-mentioned feature could be realized with the NOx adsorption catalyst which contains the element more than a kind chosen from a potassium (K), sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium) at least as a part of component.

[0027] At least the exhaust gas purge of the internal combustion engine of this invention A potassium (K), The NOx adsorption catalyst which contains the element more than a kind chosen from sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium) as a part of component is arranged to exhaust gas passage. In the oxidation reduction stoichiometry relation between each component in exhaust gas, build a state with many oxidizers to a reducing agent, and NOx is made to chemisorb on an adsorption catalyst. Next, to an oxidizer, a reducing agent builds the state more than the amount of said, catalytic reaction of the NOx which adsorbed on the adsorption catalyst is carried out to a reducing agent, and it is N2. It returns and is characterized by making it harmless.

[0028] At least the exhaust gas purge of the internal combustion engine of this invention again A potassium (K), The NOx adsorption catalyst which contains the element more than a kind chosen from sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium) as a part of component is arranged to exhaust gas passage. a oxidation reduction stoichiometry relation -- setting -- reducing agents, such as HC, -- receiving -- O2 Build a state with many oxidizers and NOx is caught by the chemical bond near an adsorption catalyst front face and the front face. etc. -- next, an oxidizer -- receiving -- a reducing agent -- the amount of said -- or many states are built and catalytic reaction of the NOx caught by the adsorption catalyst is carried out to a reducing agent -- making -- N2 It returns and is characterized by making it harmless.

[0029] Especially as a NOx adsorption catalyst in this invention, the following can apply suitably.

[0030] The constituent which consists of the metal and metallic oxide (or multiple oxide) which contain at least a kind of element chosen from the noble metals which are chosen from the rare earth which is chosen from a potassium (K), sodium (Na), magnesium (Mg), strontium (Sr), and calcium (calcium), and which serves as a kind from a cerium etc. at least, and which serve as a kind from platinum, a rhodium, palladium, at least, the constituent which comes to support this constituent to a porosity thermal-resistance metallic oxide This constituent has the SOx-proof nature which was excellent in addition to the outstanding NOx adsorption capacity.

[0031] the oxidizer in the method of this invention -- receiving -- a reducing agent -- the amount of said -- or many states can be made by the following methods

[0032] The combustion conditions in an internal combustion engine are used as theoretical air fuel ratio or overfuel (rich). Moreover, a reducing agent is added to RIN barn exhaust gas.

[0033] The former can be attained by the following methods.

[0034] How to control fuel oil consumption according to an oxygen density sensor output, an inhalation-of-air flow rate sensor output, etc. which were prepared in the jet pipe. by this method, make superfluous [ fuel ] a part of two or more cylinders, and fuel is insufficient in the remainder -- carrying out -- the component in the mixed exhaust gas from all cylinders -- a oxidation reduction stoichiometry relation -- setting -- an oxidizer -- receiving -- a reducing agent -- the amount of said -- or the method of building many states is also included

[0035] The latter can be attained by the following all directions methods.

[0036] How to throw a reducing agent into the adsorption catalyst upstream of an emission. The gasoline as fuel for an internal combustion engine, gas oil, lamp oil, natural gas, these reforming objects, hydrogen, alcohols, ammonia, etc. are applicable to a reducing agent.

[0037] It is also effective to throw in reducing agents, such as a hydrocarbon which leads a blow-by gas and canister purge gas to the adsorption catalyst upstream, and is contained in these. In a fuel direct injection formula internal combustion engine, it is effective to inject fuel like an exhaust air line and to throw in the fuel as a reducing agent.

[0038] The adsorption catalyst in this invention is applicable in various kinds of configurations. The honeycomb configuration which coats with an adsorption catalyst component the honeycomb-like structure which consists of metallic materials, such as a cordierite and stainless steel, and is acquired is made into the start, and it can apply as the shape of a pellet, a tabular, a grain, and powder.

[0039] the oxidizer in this invention -- receiving -- a reducing agent -- the amount of said -- or the timing which makes many states can be based on the following all directions methods

[0040] When the NOx discharge at the time of RIN operation is presumed from the air-fuel ratio setpoint signal determined by ECU (Engine Control Unit), an engine speed signal, an inhalation air-content signal, a pressure-of-induction-pipe force signal, a speed signal, throttle opening, exhaust gas temperature, etc. and the integrated value exceeds the predetermined set point.

[0041] When the signal of the oxygen sensor (or A/F sensor) put on the adsorption catalyst upstream or the slipstream of exhaust air passage detects the amount of accumulation oxygen and the amount of accumulation oxygen exceeds a predetermined amount. When the amount of accumulation oxygen at the time of RIN operation exceeds a predetermined amount as the deformation mode.

[0042] When the amount of accumulation NOx(es) is computed with the NOx sensor signal put on the adsorption catalyst upstream of exhaust air passage and the amount of accumulation NOx(es) at the time of RIN operation exceeds a predetermined amount.

[0043] the time of the signal of the NOx sensor put on the adsorption catalyst slipstream of exhaust air passage detecting the NOx concentration at the time of RIN operation, and NOx concentration exceeding predetermined concentration

[0044] the oxidizer in this invention -- receiving -- a reducing agent -- the amount of said -- or although time to maintain many states or the amount of reducing agents supplied that it should maintain can be beforehand decided like the above-mentioned in consideration of the property of an adsorption catalyst, an item, a property of an internal combustion engine, etc., these adjust a stroke, the injection time, and the injection interval of a fuel injection valve, and can realize it

[0045]

[Embodiments of the Invention] The concrete embodiment of this invention is mentioned and this invention is explained in detail. In addition, it cannot be overemphasized by this invention that it is not limited to the following embodiments and examples, and various kinds of embodiments are in the thought within the limits.

[0046] The property of the adsorption catalyst by the method of a [adsorption catalyst] this invention is explained. The property of N-N9 which contains Na as an alkali metal, and N-K9 containing K obtained

following <<adsorption catalyst method-of-preparation>> adsorption catalyst N-N9 by the following methods.

[0047] The alumina sol as a binder which carried out nitric-acid \*\*\*\* of alumina powder and the boehmite, and obtained them was mixed, and the nitric-acid alumina slurry was obtained. After carrying out the air blow and removing the liquid blockaded in the cell, after flooding a honeycomb with this coating liquid, it pulled up promptly, and it dried, and it calcinated at 450 degrees C continuously. This operation was repeated and the alumina of apparent-volume 1L per 150g of a honeycomb was coated. Catalytic activity component support was carried out at this alumina coat honeycomb, and the honeycomb-like adsorption catalyst was acquired. For example, it sank in and the cerium-nitrate (nitric acid Ce) solution was calcinated at 600 degrees C after dryness for 1 hour. Then, it sank in, and similarly, it dried and the mixed solution of a sodium-nitrate (nitric acid Na) solution, a titania sol solution, and a magnesium-nitrate (nitric acid Mg) solution was calcinated. Furthermore it sank into the mixed solution of a JINITO diammine Pt nitric-acid solution and a nitric-acid rhodium (nitric acid Rh) solution, and calcinated at 450 degrees C after dryness for 1 hour. Finally, it sank in and the nitric-acid Mg solution was calcinated at 450 degrees C for 1 hour. The honeycomb-like adsorption catalyst which supported Ce, Mg, Na, Ti, Rh, and Pt to the alumina (aluminum 2O3) by the above, and 2Mg-(0.2Rh, 2.7Pt)-(18Na, 4Ti, 2Mg)-27 Ce/aluminum 2O3 were obtained. Here, /aluminum 2O3 shows that it was supported on aluminum 2O3, and its active ingredient is the weight (g) of the display metal component which supported the numeric value in front of the symbol of element to per [ honeycomb apparent-volume 1L ]. Notation sequence showed support sequence, it supported in order of the component which separates from the component by which the notation will be carried out soon at aluminum 2O3, and the component bundled by ( ) was supported simultaneously. Incidentally the amount of support of each active ingredient is changeable by changing the active-ingredient concentration in a sinking-in solution.

[0048] Adsorption catalyst N-K9 was prepared by the following methods.

[0049] Using a potassium-nitrate (nitric acid K) solution instead of the nitric-acid Na solution in adsorption catalyst N-N9 manufacture, others are N-K9 with the same method as adsorption catalyst N-N9. 2Mg-(0.2Rh, 2.7Pt)-(18K, 4Ti, 2Mg)-27 Ce/aluminum 2O3 was obtained. Moreover, it is comparison catalyst N-R2 with the same method. 2Mg-(0.2Rh, 2.7Pt)-27 Ce/aluminum 2O3 was obtained.

[0050] <<performance appraisal method>> After heat-treating the adsorption catalyst acquired by the above-mentioned method by the oxidizing atmosphere at 700 degrees C for 5 hours, the following methods estimated the property.

[0051] Displacement 1.8L Capacity 1.7L prepared by the method of this invention in the passenger car which carried the RIN barn specification gasoline engine The honeycomb-like adsorption catalyst was carried and the NOx purification property was evaluated.

[0052] Property>> of <<adsorption catalyst Adsorption catalyst N-N9 is carried and it is A/F=13.3. For [ rich operation ] 30 seconds and for [ of A/F=22 / RIN operation ] about 20 minutes were repeated by turns, and the rate passage-of-time property of NOx purification of drawing 2 was acquired. it should hear from this drawing that NOx in a RIN operating period is purified by this adsorption catalyst -- \*\* The rate of purification which the rate of RIN on-stream NOx purification fell gradually, and had 100% in early stages becomes about 40% after 20 minutes. However, this lowered rate of purification is recovered even to 100% by rich operation for 30 seconds. If RIN operation is performed again, NOx decontamination capacity will be recovered and will repeat the above-mentioned aging. Even if it carries out the multiple-times loop of RIN operation and the rich operation, the speed of the decline with the passage of time in the rate of NOx purification under RIN operation is eternal, and this shows that NOx adsorptivity ability was fully reproduced by rich operation.

[0053] The vehicle speed was considered as about 40 km [h ] regularity ((space-velocity simian virus) about 20,000-/h regularity of exhaust gas), ignition timing was changed, the NOx concentration in exhaust gas was changed, and drawing 3 was obtained in quest of the relation between NOx concentration and the rate of NOx purification in RIN exhaust gas. Although the rate of NOx purification falls with time, fall speed has NOx concentration as small as a low. It will become Table 1 if

the amount of NO<sub>x</sub>(es) caught by the time it resulted to 50% of rates of NO<sub>x</sub> purification and 30% is calculated from this drawing.

[0054] The amount of NO<sub>x</sub> prehension does not depend on NO<sub>x</sub> concentration, but is simultaneously regularity. It is the feature of chemical absorption that the amount of adsorption does not approach the concentration (pressure) of an adsorbate.

[0055] Pt particle is first thought as a NO<sub>x</sub> adsorbent in a sample offering adsorption catalyst. When CO amount-of-adsorption evaluation which evaluates the amount of exposure Pt(s) and which is used abundantly as a means was performed, CO amount of adsorption (at 100 degree C) was  $4.5 \times 10^{-4}$  mol. This value is about 1 of the above-mentioned NO<sub>x</sub> amount of adsorption/100, and it is clear that Pt is not the leading role of a NO<sub>x</sub> adsorbent.

[0056] the BET specific surface area (it measures by nitrogen adsorption) measured the whole cordierite of this adsorption catalyst on the other hand -- about 25m<sup>2</sup>/g -- per [ honeycomb 1.7L ] -- it was 28,050m<sup>2</sup>. Moreover, when the chemical structure of Na of the adsorption catalyst of this invention was examined, it is CO<sub>2</sub> to a mineral acid. It has been judged that it mainly existed as Na<sub>2</sub>CO<sub>3</sub> judging from the value of the point of inflection in the neutralization-titration curve by generating gas and dissolving and the mineral acid. Supposing all front faces are occupied by Na<sub>2</sub>CO<sub>3</sub>, 0.275-mol Na<sub>2</sub>CO<sub>3</sub> will be exposed to a front face (since the specific gravity of Na<sub>2</sub>CO<sub>3</sub> is 2.533g/ml, the volume of Na<sub>2</sub>CO<sub>3</sub> 1 molecule can be found (Na<sub>2</sub>CO<sub>3</sub> was assumed to be a cube and this was made into the occupancy area of surface Na<sub>2</sub>CO<sub>3</sub> in quest of the area of the 1st page).). If the above-mentioned reaction formula is followed, 0.275-mol Na<sub>2</sub>CO<sub>3</sub> will be 0.55-mol NO<sub>2</sub>. There is capacity to adsorb. However, the amount of NO<sub>x</sub>(es) which the adsorption catalyst of this invention actually removed is the 1/10 or less 0.04-mol order. This difference is because a BET adsorption method evaluates a physical surface area and is also evaluating surface areas other than Na<sub>2</sub>CO<sub>3</sub> of aluminum<sub>2</sub>O<sub>3</sub> grade. The above evaluation has few amounts of adsorption NO<sub>x</sub>(es) farther than the NO<sub>x</sub> prehension ability of Na<sub>2</sub>CO<sub>3</sub> bulk, and it is shown that NO<sub>x</sub> is caught at least in the field in which it was restricted Na<sub>2</sub>CO<sub>3</sub> front face or near the front face.

[0057] In drawing 3, the aforementioned NO<sub>x</sub> adsorption capacity force declines with the increase in the mileage of an automobile, and the reduction speed of the rate of NO<sub>x</sub> purification after changing from SUTOIKI operation to RIN operation becomes quick. This is for the poisoning objects (SO<sub>x</sub> etc.) contained in exhaust gas reacting with a NO<sub>x</sub> adsorbate, and reducing the adsorption capacity force. This degradation can make it recover by eliminating from a catalyst the poisoning object of the catalyst accumulated with time by making into the state of theoretical air fuel ratio or overfuel (rich) the exhaust air discharged from an internal combustion engine, and holding an exhaust-gas temperature more than a predetermined period more than predetermined.

[0058] Drawing 4 shows the rate of NO<sub>x</sub> purification immediately after changing from RIN operation to SUTOIKI operation. With this adsorption catalyst, it turns out that 90% or more of rate of NO<sub>x</sub> purification is obtained from immediately after changing to SUTOIKI operation.

[0059] The NO<sub>x</sub> purification property before and behind SUTOIKI or the change through which it passes richly was shown in drawing 5 and drawing 6 from RIN. Drawing 5 is what showed the NO<sub>x</sub> concentration of the entrance of adsorption catalyst N-N9, and an outlet, and drawing (a) is A/F=14.2 from RIN of A/F=22. It is the case where passed and an air-fuel ratio is changed, richly. It sets at the start time of reproduction immediately after a rich change, and is A/F=14.2. Although the entrance NO<sub>x</sub> concentration of rich operation increases greatly and outlet NO<sub>x</sub> concentration increases transitionally in connection with this since exhaust gas NO<sub>x</sub> concentration is high, outlet NO<sub>x</sub> concentration is always much less than entrance NO<sub>x</sub> concentration. In reproduction, outlet NO<sub>x</sub> concentration reaches about zero in a lead short time promptly. Although drawing (b) is a case which is A/F=14.2 from RIN of A/F=22 where passed richly and an air-fuel ratio is changed, like drawing (a), outlet NO<sub>x</sub> concentration is always much less than entrance NO<sub>x</sub> concentration, and outlet NO<sub>x</sub> concentration reaches about zero more for a short time.

[0060] As mentioned above, although it is clear, A/F value as reproduction conditions influence at the time which reproduction takes. The amount of reducing agents is further influenced A/F value suitable

for reproduction, and time of composition of an adsorption catalyst, a configuration, temperature, space velocity, the kind of reducing agent, the configuration of exhaust air passage, or length. Therefore, reproduction conditions are synthetically decided in consideration of these.

[0061] Drawing 6 is what showed the NOx concentration of the entrance of adsorption catalyst N-K9, and an outlet, and drawing (a) is  $A/F=14.2$  from RIN of  $A/F=22$ . When it passes richly and an air-fuel ratio is changed, drawing (b) is  $A/F=14.2$  from RIN of  $A/F=22$ . Although it is the case where passed and an air-fuel ratio is changed, richly Like the case of above-mentioned adsorption catalyst N-N9, always, outlet NOx concentration is much less than entrance NOx concentration, and reproduction of an adsorption catalyst is progressing for a short time.

[0062] [Exhaust air purification control unit] drawing 1 is the whole equipment composition which shows one embodiment of the exhaust gas purification control unit of this invention.

[0063] The equipment of this invention consists of exhaust air systems, control units (ECU), etc. which have the engine 99 in which a RIN barn is possible, an intake air flow sensor 2, the inhalation-of-air system which has electronics control throttle-valve 3 grade, the oxygen density sensor (or A/F sensor) 19, the exhaust air thermo sensor 17, and NOx adsorption catalyst 18 grade. ECU is I/O as an input/output interface. It consists of Storage RAM and ROM, timer counters, etc. which made the control program of LSI, a processing unit MPU, and a large number memorize. The above exhaust air purification control unit functions as follows. The inhalation air to an engine is measured by the back intake air flow sensor 2 filtered with the air cleaner 1, receives fuel injection from an injector 5 further through the electronics control throttle valve 3, and is supplied to an engine 99 as a gaseous mixture. The sensor signal of an intake air flow sensor signal and others is inputted into ECU (Engine Control Unit).

[0064] In ECU, the operational status of an internal combustion engine and the state of a NOx adsorption catalyst are evaluated, an operation air-fuel ratio is determined, the injection time of an injector 5 etc. is controlled by the below-mentioned method, and the fuel concentration of a gaseous mixture is set as a predetermined value by it. Moreover, you may set the fuel concentration of a gaseous mixture as a predetermined value by opening adjustment of the electronics control throttle valve 3. The gaseous mixture inhaled by the cylinder is lit by the ignition plug 10 controlled by the signal from ECU25, and burns. A combustion gas is led to an exhaust air purification system. The combustion function which it has at the same time a NOx adsorption catalyst is prepared in an exhaust air purification system, and the three-way-component-catalyst function purifies NOx, HC, and CO in exhaust gas at the time of SUTOIKI operation and NOx adsorption capacity purifies NOx at the time of RIN operation purifies HC and CO. Furthermore, when the NOx decontamination-capacity force of a NOx adsorption catalyst is always judged at the time of RIN operation and the NOx decontamination-capacity force declines with a judgment and control signal of ECU, the air-fuel ratio of combustion etc. is shifted to a rich side, and the NOx adsorption capacity of an adsorption catalyst is recovered. The above operation purifies effectively the exhaust gas under all the engine combustion conditions of RIN operation and SUTOIKI (rich [ contain and ]) operation with this equipment.

[0065] The fuel concentration (following air-fuel ratio) of the gaseous mixture supplied to an engine is controlled as follows. The block diagram showed the AFC method to drawing 7.

[0066] ECU25 determines an air-fuel ratio (A/F) from information, such as the output signal of the amount of inhalation of air measured by the load sensor output which outputs the signal according to treading in to an accelerator pedal, and the intake air flow sensor, an engine speed signal detected by the crank angle sensor, an exhaust gas temperature signal, a throttle sensor signal which detects throttle opening, an engine-coolant water temperature signal, and a starter signal, and further, this signal is amended based on the signal fed back from an oxygen sensor, and determines fuel oil consumption. In addition, in the time of a heavy load, feedback control is suspended with the signal of each sensor and a switch at the time of an idle at the time of low temperature. Moreover, it corresponds by the air-fuel ratio amendment learning function so that it can respond also to a delicate change and a sudden change of an air-fuel ratio correctly by the air-fuel ratio amendment learning function.

[0067] SUTOIKI ( $A/F=14.7$ ) and when it is rich ( $A/F<14.7$ ), the injection conditions of an injector are

determined for the determined air-fuel ratio by directions of ECU, and SUTOIKI and rich operation are performed. Opening adjustment of the electronics control throttle valve 3 may perform SUTOIKI and rich operation. On the other hand, when judged with existence of the NOx adsorption capacity of a NOx adsorption catalyst being judged, and there being adsorption capacity, when RIN ( $A/F > 14.7$ ) operation is determined, fuel oil consumption is determined to perform RIN operation as directed, when judged with there being no adsorption capacity, the predetermined period rich shift of the air-fuel ratio is carried out, and a NOx adsorption catalyst is reproduced. You may perform RIN operation by opening the electronics control throttle valve 3 and making an inhalation air content increase.

[0068] Whenever the integrated value of every predetermined mileage and an inhalation air content exceeds the specified quantity in addition to regeneration of the aforementioned NOx adsorption catalyst, it operates by service condition which an exhaust-gas temperature becomes more than predetermined. The NOx adsorption capacity force in which it deteriorated by the poisoning accumulation of substance can be recovered by adding this processing. As a means to raise an exhaust-gas temperature, the electronics control throttle valve 3 which delays ignition timing is opened, and there is the method of returning to SUTOIKI of carrying out a flame failure and raising the internal temperature of a catalyst etc., from RIN to which an inhalation air content is made to increase and which introduces secondary air into an exhaust pipe.

[0069] The flow chart of the recovery at the time of the aforementioned poisoning was shown in drawing 8 (a).

[0070] The flow chart of AFC was shown in drawing 8 (b). Or it directs various kinds of service conditions at Step 1002, the signal which detects operational status is read. The air-fuel ratio determined by determination and Step 1004 in the air-fuel ratio at Step 1003 based on these signals is detected. The size of the air-fuel ratio and theoretical air fuel ratio which were determined at Step 1005 is compared. The theoretical air fuel ratio used as the candidate for comparison here is an air-fuel ratio to which the speed of the catalytic-reduction reaction of NOx exceeds the capture velocity by adsorption in an adsorption catalyst correctly, the property of an adsorption catalyst is evaluated beforehand, it is determined, and the air-fuel ratio near the theoretical air fuel ratio is selected. Here, air-fuel ratio operation as directed is performed, without progressing to Step 1006 in the case of setting air-fuel ratio  $\leq$  theoretical air fuel ratio, and performing reproduction operation of an adsorption catalyst. In the case of setting air-fuel ratio  $>$  theoretical air fuel ratio, it progresses to Step 1007. At Step 1007, the presumed operation of the NOx amount of adsorption is performed. About the presumed operation method, it mentions later. Then, it judges whether the presumed NOx amount of adsorption is below a predetermined critical mass at Step 1008. The marginal amount of adsorption is set as the value which evaluates the NOx prehension property of an adsorption catalyst by experiment etc. beforehand, and NOx in exhaust gas can fully purify in consideration of exhaust gas temperature, the degree of adsorption catalyst temperature, etc. Air-fuel ratio operation as directed is performed without progressing to Step 1006 and performing reproduction operation of an adsorption catalyst, when there is NOx adsorption capacity. When there is no NOx adsorption capacity, it progresses to Step 1009, and an air-fuel ratio is shifted to a rich side. At Step 1010, rich shift time is counted, and if elapsed time  $T_r$  exceeds the predetermined time ( $T_r$ ) c, a rich shift will be ended.

[0071] The judgment of NOx adsorption capacity can be performed as follows.

[0072] Drawing 9 is the method of integrating and judging a NOx discharge from the various service conditions at the time of RIN operation.

[0073] Step 1007- The amount EN of NOx(es) to which the signal about the operation conditions of NOx adsorption catalysts, such as exhaust gas temperature, and the signal about various kinds of engine service conditions which influence the NOx concentration in exhaust gas are read into by E01, and it sticks at unit time It guesses. Step 1007- It is EN at E02. It integrates and is integrated-value  $\sigma EN$  at step 1008-E01. Size with the upper limit (EN) c of the amount of adsorption is compared. In  $\sigma EN \leq (EN) c$ , addition is continued, in  $\sigma EN > (EN) c$ , it cancels addition by step 1008-E02, and progresses to Step 1009.

[0074] Drawing 10 is the method of judging in addition time of RIN operation.



[0075] Step 1007- It is the operation time HL of RIN at H01. It integrates and is integrated-value sigmaHL at step 1008-H01. Upper limit of addition time Size with (HL) c is compared.  $\text{sigmaHL} \leq (\text{HL}) c$  a case -- addition -- continuing -- the case of  $\text{sigmaHL} > (\text{HL}) c$  -- step 1008- addition is canceled by H02 and it progresses to Step 1009

[0076] Drawing 11 is the method of judging by the oxygen-sensor signal at the time of RIN operation.

[0077] Step 1007- The amount [ in / RIN operation / at O01 ] QO of oxygen It integrates and is integrated-value sigmaQO at step 1008-O01. Size with the upper limit (QO) c of the amount of addition oxygen is compared. In  $\text{sigmaQO} \leq (\text{QO}) c$ , addition is continued, in  $\text{sigmaQO} > (\text{QO}) c$ , addition is canceled by step 1008-O02, and it progresses to Step 1009.

[0078] Drawing 12 is the method of judging by the NOx concentration sensor signal detected at the NOx adsorption catalyst entrance at the time of RIN operation.

[0079] Step 1007- Based on a NOx concentration sensor signal, the amount QN of NOx(es) in a NOx adsorption catalyst entrance is integrated by N01. Step 1008- N01 compares size with the upper limit (QN) c of integrated-value sigmaQN and the amount of addition NOx(es).  $\text{sigmaQN} \leq (\text{QN}) c$  a case -- addition -- continuing --  $\text{sigmaQN} > (\text{QN}) c$  a case -- step 1008- addition is canceled by N02 and it progresses to Step 1009

[0080] Drawing 13 is the method of judging by the NOx concentration sensor signal detected at the NOx adsorption catalyst outlet at the time of RIN operation.

[0081] Step 1007- NOx concentration [ in / a NOx adsorption catalyst entrance / based on a NOx concentration sensor signal / at C01 ] CN It detects. Step 1008- C01 compares size with the upper limit (CN) c of CN and CN. the case of  $\text{CN} \leq (\text{CN}) c$  -- detection -- continuing --  $\text{CN} > (\text{CN}) c$  a case -- Step 1009 -- progressing .

[0082] Other embodiments of the exhaust gas purge of this invention are shown in drawing 14 . The point of having formed the manifold catalyst 17 in the jet pipe near the engine has the difference with the mode of drawing 1 . Strengthening of eccrisis regulation of automobile exhaust needs purification of detrimental objects, such as HC discharged immediately after engine starting. That is, although it was unsettled and was conventionally discharged until the catalyst reached operation temperature, it is necessary to reduce this amount sharply. The method of carrying out the temperature up of the catalyst quickly to operation temperature is effective in this. Drawing 14 is the equipment configuration which can respond to the exhaust gas purification in HC of engine during starting, CO discharge reduction, and RIN and SUTOIKI (rich [ contain and ]) operation. It sets in the composition of drawing 14 and is Pt, Rh, and CeO<sub>2</sub> in the manifold catalyst 17. The combustion catalyst which added Pd or used combustion active ingredients, such as Pd, as the main component is applicable to the so-called three way component catalyst and these so-called which are made into a main component. With this composition, the manifold catalyst 17 carries out a temperature up to during starting for a short time, purification of HC or CO is performed from immediately after starting, at the time of SUTOIKI operation, the both sides of a manifold catalyst and the adsorption catalyst 18 function, HC, CO, and NOx are purified, and an adsorption catalyst carries out adsorption purification of the NOx at the time of RIN operation. If the rich shift of the air-fuel ratio is carried out in reproduction of an adsorption catalyst, HC as a reducing agent and CO will reach an adsorption catalyst, without receiving a big chemical change with a manifold catalyst, and will reproduce this. enabling such composition -- the size of an adsorption catalyst -- it comes and they are 7s features

[0083] The embodiment of further others of the exhaust gas purge of this invention is shown in drawing 15 . The point that an engine 99 is a cylinder-injection-of-fuel method has the difference with the mode of drawing 1 . The equipment of this invention is applicable also to a cylinder-injection-of-fuel method engine good.

[0084] The embodiment of further others of the exhaust gas purge of this invention is shown in drawing 16 . Having formed the back catalyst 24 in the lower stream of a river of an adsorption catalyst has the difference with the mode of drawing 1 and drawing 15 . For example, the equipment with which the equipment which raised HC decontamination capacity made the 3 yuan function at the time of SUTOIKI strengthen by placing a three way component catalyst is realized by putting a combustion catalyst on a



back catalyst.

[0085] The embodiment of further others of the exhaust gas purge of this invention is shown in drawing 17. Adding fuel for the adsorption catalyst upstream through the reducing-agent injector 23 has the difference with drawing 1 and drawing 14 - drawing 16 with directions of a rich shift. By this method, there is a big advantage that the operational status of an engine can be set up regardless of the state of an adsorption catalyst.

[0086] When adsorption catalyst N-N9 by the method of this invention was carried in drawing 18 and adsorption catalyst N-K9 was carried, the NOx concentration before and behind the adsorption catalyst in the 10 modes of the last in the 10 modes repeated 3 times at the time of carrying comparative catalyst N-R2 and the 15 modes following it was shown. The comparison catalyst was made into the thing of the composition shown in Table 2 of back \*\*.

[0087] In drawing 18, it turns out that an adsorption catalyst is reproduced effectively and outlet NOx concentration is less than entrance NOx concentration in all operation regions when adsorption catalyst N-N9 and N-K9 are carried, and hold a NOx purification function is being continued by repeating RIN operation and SUTOIKI operation. On the other hand, the portion into which outlet NOx concentration exceeds entrance NOx concentration in comparison catalyst N-R2 has arisen.

[0088] The CVS value acquired with various adsorption catalysts and the comparison catalyst was shown in Table 2 and 3 with adsorption catalyst composition. Although manufacture of an adsorption catalyst and a comparison catalyst was based on the above-mentioned method, as a manufacture raw material, the nitric acid Ba was used for barium (Ba), and the silica sol was used for silicon (Si). It is presumed that Si exists as a silica (SiO<sub>2</sub>) or its multiple oxide.

[0089] As mentioned above, according to the equipment of this invention, by preparing a NOx adsorption catalyst in exhaust gas passage, carrying out adsorption prehension of the NOx by the oxidizing atmosphere of RIN exhaust gas, building reducing atmosphere, and reproducing an adsorption catalyst, without having big influence on mpg, it is efficient and NOx in RIN barn exhaust gas etc. can be purified so that clearly.

[0090]

[Table 1]

表 1

入口排ガス中 NOx濃度(ppm)	浄化率50%になるまでに 浄化したNOx量 (mol)	浄化率30%になるまでに 浄化したNOx量 (mol)
約 50 ppm	0.030	0.041
約120 ppm	0.031	0.047
約230 ppm	0.030	0.045
約450 ppm	0.030	0.042
約550 ppm	0.026	0.038

[0091]

[Table 2]

表 2

	記 号	組 成	CVS値(g/km)		
			NOx	HC	CO
比較 触媒	N-R1	(0.2Rh, 2.7Pt) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.18	0.02	0.07
	N-R2	2Mg - (0.2Rh, 2.7Pt) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.15	0.02	0.04
吸着 触媒	N-S1	2Mg - (0.2Rh, 2.7Pt) - 30Sr - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.08	0.10	0.08
	N-S2	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 2Mg) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.09	0.08	0.08
	N-S3	(0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.11	0.08	0.11
	N-S4	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Ti) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.10	0.07	0.09
	N-S5	2Mg - (0.2Rh, 2.7Pt) - (30Sr, 4Si) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.10	0.08	0.09
	N-N1	2Mg - (0.2Rh, 2.7Pt) - 18Na - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.03
	N-N2	2Mg - (0.2Rh, 2.7Pt) - (18Na, 2Mg) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.06	0.12	0.04
	N-N3	(0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.07	0.16	0.10
	N-N4	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.06	0.15	0.08
	N-N5	(0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.08	0.10	0.12
	N-N6	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Si) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.06
	N-N7	2Mg - (0.2Rh, 2.7Pt) - (10Na, 10Sr) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.05	0.10	0.05
	N-N8	(0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.07	0.12	0.07
	N-N9	2Mg - (0.2Rh, 2.7Pt) - (18Na, 4Ti, 2Mg) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.04	0.11	0.04
	N-N10	2Mg - (0.2Rh, 2.7Pt) - (10Na, 10Sr, 2Mg) - 27Ce / Al <sub>2</sub> O <sub>3</sub>	0.04	0.06	0.04

[0092]

[Table 3]

表 3

	記 号	組 成	CVS値(g/km)		
			NOx	HC	CO
吸着 触媒	N-K1	2Mg-(0.2Rh, 2.7Pt)-18K-27Ce/ $Al_2O_3$	0.06	0.08	0.03
	N-K2	2Mg-(0.2Rh, 2.7Pt)-(18K, 2Mg)-27Ce/ $Al_2O_3$	0.05	0.10	0.05
	N-K3	(0.2Rh, 2.7Pt)-(18K, 4Ti)-27Ce/ $Al_2O_3$	0.08	0.11	0.06
	N-K4	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Ti)-27Ce/ $Al_2O_3$	0.05	0.08	0.05
	N-K5	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Si)-27Ce/ $Al_2O_3$	0.06	0.08	0.05
	N-K6	(0.2Rh, 2.7Pt)-(18K, 10Sr)-27Ce/ $Al_2O_3$	0.07	0.12	0.06
	N-K7	2Mg-(0.2Rh, 2.7Pt)-(18K, 10Sr)-27Ce/ $Al_2O_3$	0.05	0.10	0.05
	N-K8	(0.2Rh, 2.7Pt)-(18K, 4Ti, 2Mg)-27Ce/ $Al_2O_3$	0.06	0.10	0.07
	N-K9	2Mg-(0.2Rh, 2.7Pt)-(18K, 4Ti, 2Mg)-27Ce/ $Al_2O_3$	0.05	0.07	0.04
	N-K10	2Mg-(0.2Rh, 2.7Pt)-(10K, 10Sr, 2Mg)-27Ce/ $Al_2O_3$	0.04	0.07	0.06
	N-M1	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 4Ti)-27Ce/ $Al_2O_3$	0.05	0.06	0.08
	N-M2	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 10Si)-27Ce/ $Al_2O_3$	0.06	0.08	0.08
	N-M3	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 10Sr)-27Ce/ $Al_2O_3$	0.06	0.10	0.05
	N-M4	2Mg-(0.2Rh, 2.7Pt)-(10Na, 10K, 4Ti, 2Mg)-27Ce/ $Al_2O_3$	0.05	0.11	0.05

[0093]

[Effect of the Invention] Since an exhaust-gas temperature is operated by the service condition of a predetermined value whenever the integrated value of every predetermined mileage and an inhalation air content exceeds a predetermined value according to this invention, even if a NOx adsorption catalyst carries out poisoning by the sulfur content contained in fuel and adsorptivity ability deteriorates, the NOx adsorption capacity force in which the poisoning accumulation of substance was canceled and it deteriorated can be recovered. Consequently, poisoning-proof nature improves, it is efficient and NOx has been purified for a long time.

[Translation done.]

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## PRIOR ART

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[Description of the Prior Art] The carbon monoxide (CO) and hydrocarbon (HC:Hydrocarbon) which are contained in the exhaust gas discharged from internal combustion engines, such as an automobile, nitrogen oxide (NOx), etc. have a bad influence on a human body as an air pollution substance, and also occur problems, such as barring growth of vegetation. Then, from before, great efforts were paid to these discharge reduction, in addition to reduction of the yield by the improvement of the combustion method of an internal combustion engine, development of the method of purifying the discharged exhaust gas using a catalyst etc. was furthered, and the steady result has been mentioned. a gasoline engine vehicle -- being related -- a three way component catalyst -- the method using the catalyst which makes Pt and Rh the principal component of activity, performs oxidization of HC and CO and reduction of NOx simultaneously, and makes them harmless is in use

[0003] By the way, a three way component catalyst acts only on the exhaust gas which was burned near the theoretical air fuel ratio called a window, and was generated from the property effectively. Then, although an air-fuel ratio is conventionally changed according to an automobilism situation, the change range has been adjusted in principle near the theoretical air fuel ratio (in the case of a gasoline, on below  $A(\text{weight of air})/F(\text{weight of fuel}) = \text{abbreviation } 14.7$ ; book specifications, although a theoretical \*\*\*\* ratio is represented with  $A/F=14.7$ , this numeric value changes with a fuel seed.). However, if an engine can be operated with an air-fuel ratio thinner (RIN) than theoretical air fuel ratio, since mpg can be raised, the automobile which development of a RIN barn combustion technology is furthered [ automobile ] and burns an internal combustion engine recently in a with an air-fuel ratios of 18 or more RIN region is not new. however -- above -- present -- business -- if RIN barn exhaust air is made to purify by the three way component catalyst, although oxidization purification of HC and CO can be performed, reduction purification of the NOx cannot be carried out effectively therefore, application to the large-size car of a RIN barn method and expansion (expansion of the application operation region of a RIN barn method) of a RIN barn burning time are advanced -- being alike -- RIN barn correspondence exhaust gas purification technology is needed Then, development of RIN barn correspondence exhaust air purification technology, i.e., the technology which purifies HC, NO, and NOx in the exhaust gas in which oxygen (O2) is contained so much, especially development of the technology which purifies NOx are furthered energetically.

[0004] In JP,63-61708,A, HC is supplied to the upstream of RIN barn exhaust gas, and it is O2 in exhaust gas. The method of lowering concentration to the concentration region where a catalyst functions effectively, and pulling out the capacity of a catalyst is proposed.

[0005] JP,62-97630,A, No. 106826 [ 62 to ], and No. 117620 [ 62 to ] are NOx in exhaust gas (NO oxidizing.). NO2 which is easy to be absorbed After changing, when the catalyst which has NOx absorbing power is made to contact, absorption removal is carried out and an absorption efficiency falls, reduction removal of the NOx which stopped passage of exhaust gas and was accumulated using reducing agents, such as HC, such as H2 and a methane gasoline, is carried out, and the method of reproducing the NOx absorbing power of a catalyst is shown.

[0006] Moreover, O2 in the exhaust gas which flows into a NOx absorbent NOx which installed in the

flueway the NOx absorbent which emits NOx absorbed when exhaust gas was RIN, NOx is absorbed to PCT/JP 92/01279 and PCT/JP 92/01330 and the oxygen density in exhaust gas was reduced to them, was made to absorb NOx when exhaust gas was RIN, and was made to absorb The exhaust emission control device to which concentration is made to fall to and is made to emit is proposed.

[0007] However, a lot of HC is needed for attaining composition (about about 0.5% of O2 concentration) of the exhaust gas equivalent to about [ which is the air-fuel ratio as which a catalyst functions in JP,63-61708,A (A/F) ] 14.7. Although use of the blow-by gas of this invention is effective, it is not sufficient amount to process the exhaust gas under internal combustion engine operation. Although it is not technically impossible to throw in fuel, either, a result to which the mpg reduced by the RIN barn method is reduced is brought.

[0008] Moreover, in order to stop circulation of exhaust gas in reproduction of a NOx absorbent and to contact reducing agents, such as HC, to a NOx absorbent in JP,62-97630,A, 62-106826, and No. 117620 [ 62 to ], it is O2 in the exhaust gas of a reducing agent. The combustion consumption to depend is suppressed sharply and the amount of the reducing agent used decreases sharply. However, the exhaust air change mechanism for preparing two NOx absorbents and circulating exhaust gas by turns to these is required, and structure of an exhaust air processor cannot deny a bird clapper intricately.

[0009] Furthermore, always circulate exhaust gas to a NOx absorbent, when exhaust gas is RIN, NOx is made to absorb in PCT/JP 92/01279 and PCT/JP 92/01330, and it is O2 in exhaust gas. In order to make NOx which concentration was reduced and absorbed it emit and to reproduce an absorbent, the change of an emission is unnecessary and the trouble of the above-mentioned method is canceled. However, when sulfur (SOx) was contained in exhaust air, the NOx absorbent combined the above catalyst with SOx, and it became a sulfide, and it had the problem that absorptance was quickly inferior.

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## DESCRIPTION OF DRAWINGS

## [Brief Description of the Drawings]

- [Drawing 1] The block diagram of the exhaust gas purge by the method of this invention which shows the typical embodiment of this invention.
- [Drawing 2] The property of the rate of NOx purification when repeating rich operation and RIN operation by turns by the method of this invention with the passage of time.
- [Drawing 3] Relation between mileage and the rate of NOx purification.
- [Drawing 4] The rate of NOx purification in SUTOIKI exhaust gas.
- [Drawing 5] Relation between the adsorption catalyst entrance NOx concentration when changing from rich (SUTOIKI) operation to RIN operation, and outlet NOx concentration.
- [Drawing 6] Relation between the adsorption catalyst entrance NOx concentration when changing from rich (SUTOIKI) operation to RIN operation, and outlet NOx concentration.
- [Drawing 7] The block diagram showing the control method of an air-fuel ratio.
- [Drawing 8] (a) is a flow chart which shows the control method of an air-fuel ratio. (b) is a flow chart which shows the control method of an air-fuel ratio.
- [Drawing 9] The flow chart which shows the NOx discharge addition judging method at the time of RIN operation.
- [Drawing 10] The amount guess portion of NOx(es) in the flow chart of drawing 8.
- [Drawing 11] The amount guess portion of NOx(es) in the flow chart of drawing 8.
- [Drawing 12] The amount guess portion of NOx(es) in the flow chart of drawing 8.
- [Drawing 13] The amount guess portion of NOx(es) in the flow chart of drawing 8.
- [Drawing 14] The block diagram of the equipment in which the embodiment which established the manifold catalyst is shown.
- [Drawing 15] The block diagram of the equipment in which the embodiment in a cylinder-injection-of-fuel engine is shown.
- [Drawing 16] The block diagram of the equipment in which the embodiment which established the back catalyst is shown.
- [Drawing 17] The equipment configuration view showing the embodiment which adds a reducing agent for the upstream of an adsorption catalyst.
- [Drawing 18] The NOx purification property view when carrying out mode operation.
- [Description of Notations]
- 1 [ -- Throttle valve, ] -- An air cleaner, 2 -- An intake air flow sensor, 3 5 [ -- An accelerator pedal, 8 / - Load sensor, ] -- An injector, 6 -- An ignition plug, 7 9 [ -- A fuel tank, 17 / -- Manifold catalyst, ] -- An intake-air-temperature sensor, 12 -- A fuel pump, 13 18 [ -- The degree sensor of adsorption catalyst temperature, ] -- An adsorption catalyst, 19 -- An oxygen sensor, 20 21 [ -- A reducing-agent injector, 24 / -- An after catalyst, 25 / -- ECU, 26 / -- A knock sensor, 28 / -- Water temperature SANSa, 29 / -- A crank angle sensor, 99 / -- Engine. ] -- An exhaust gas thermo sensor, 22 -- NOx concentration SANSa, 23

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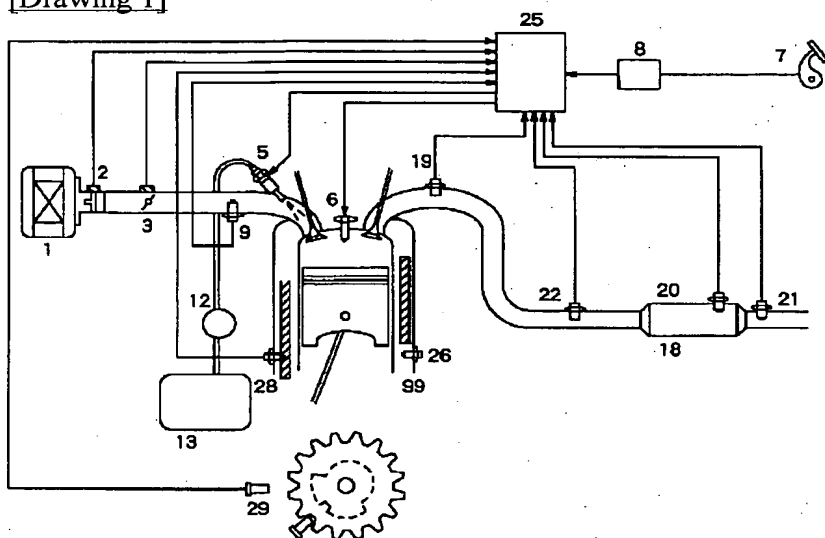
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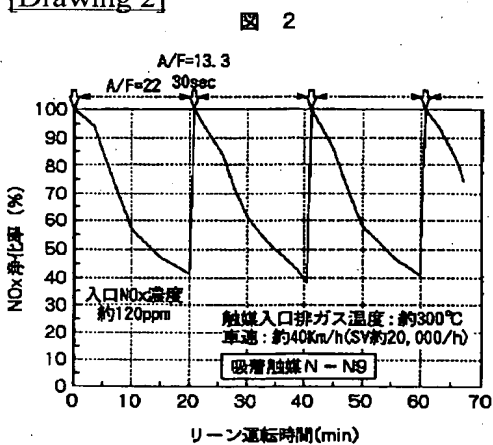
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## DRAWINGS

[Drawing 1]



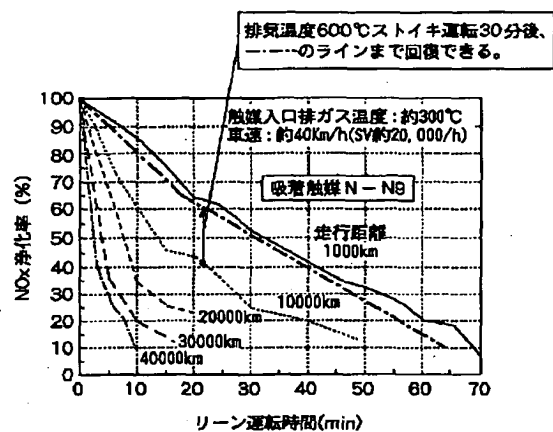
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[Drawing 3]

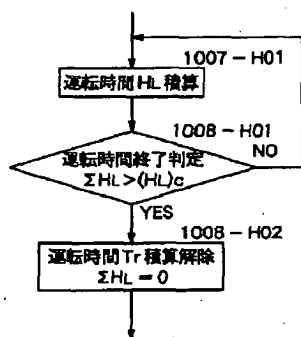


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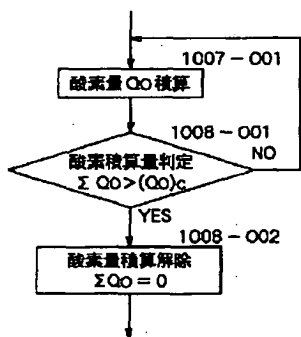
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図 10



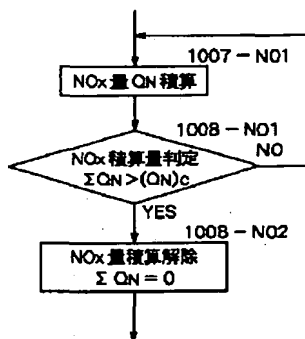
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図 11



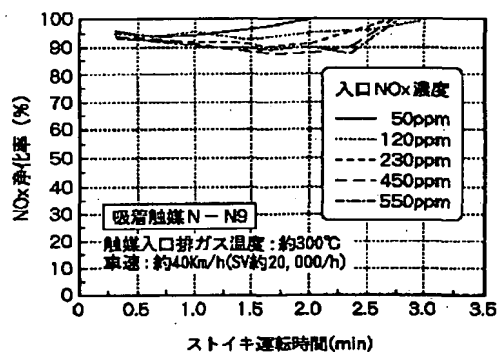
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図 12



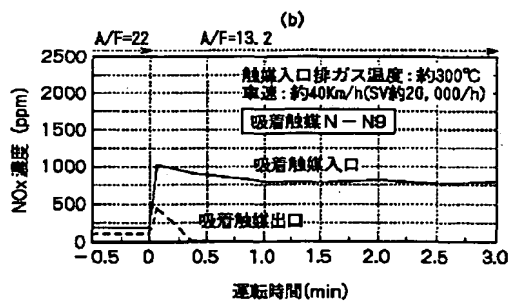
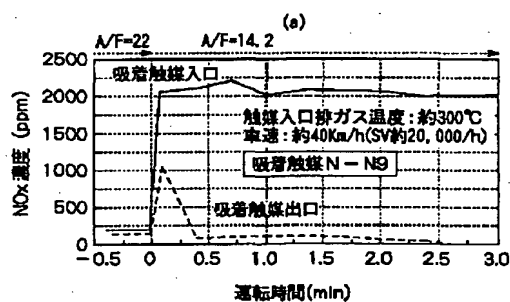
[Drawing 4]

図 4



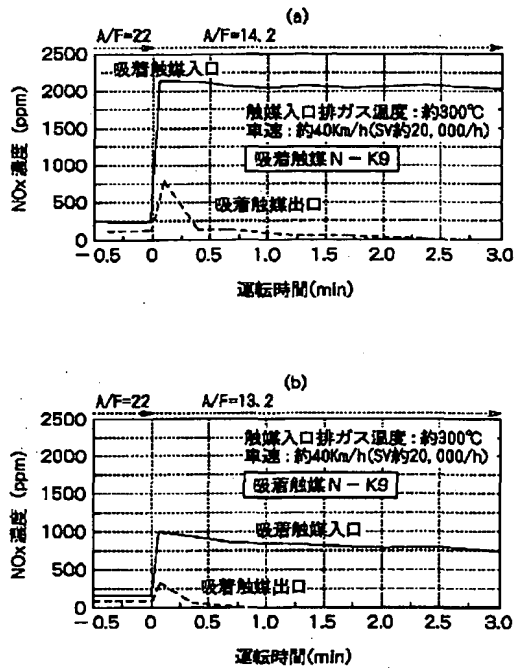
[Drawing 5]

図 5



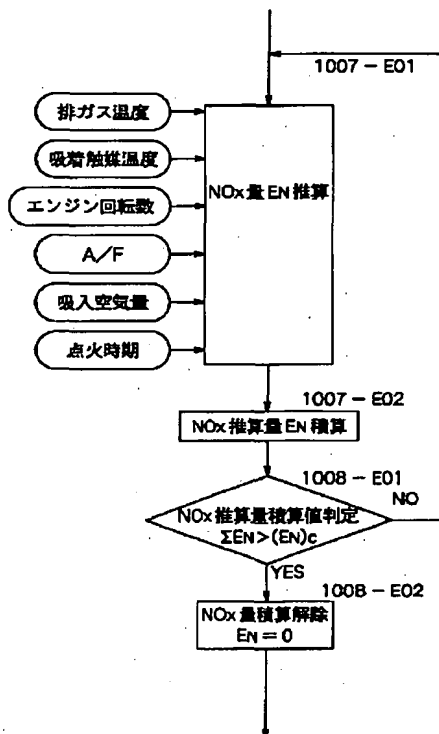
[Drawing 6]

図 6



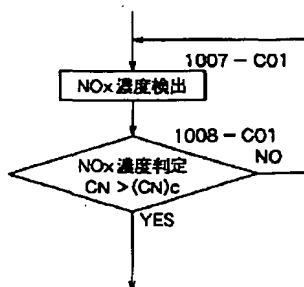
[Drawing 9]

図 9



[Drawing 13]

図 13



[Drawing 7]

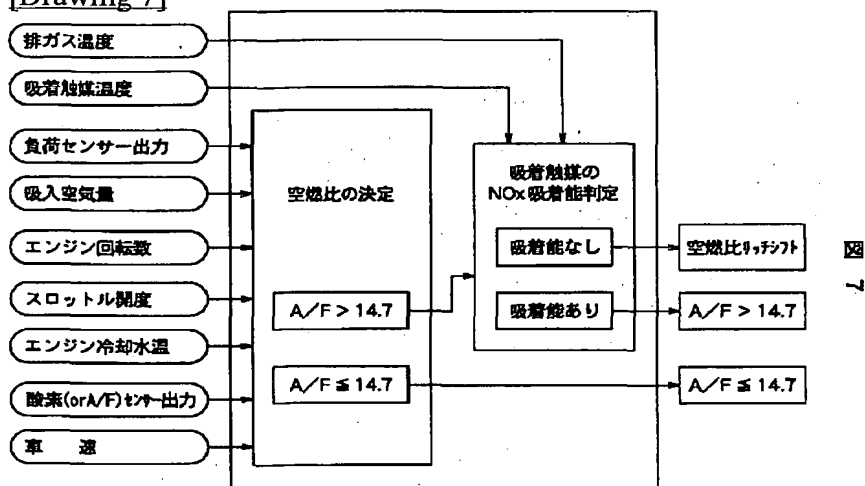


図 7

[Drawing 14]

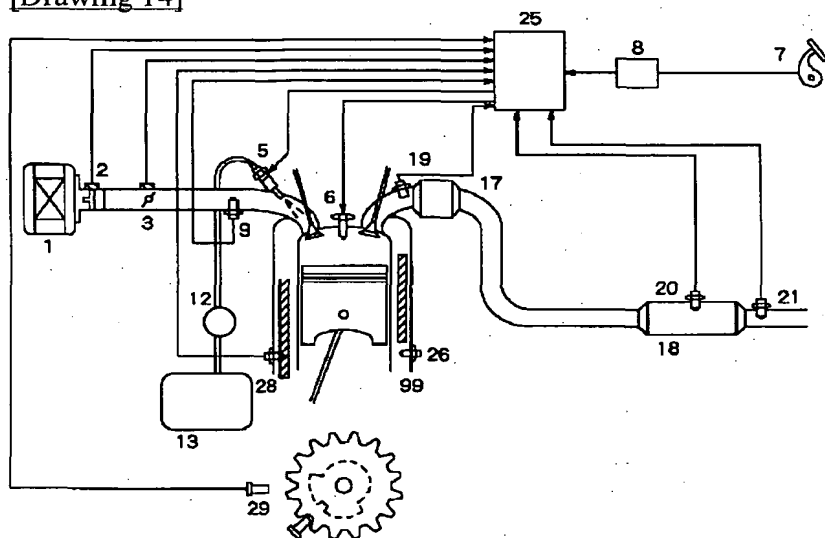
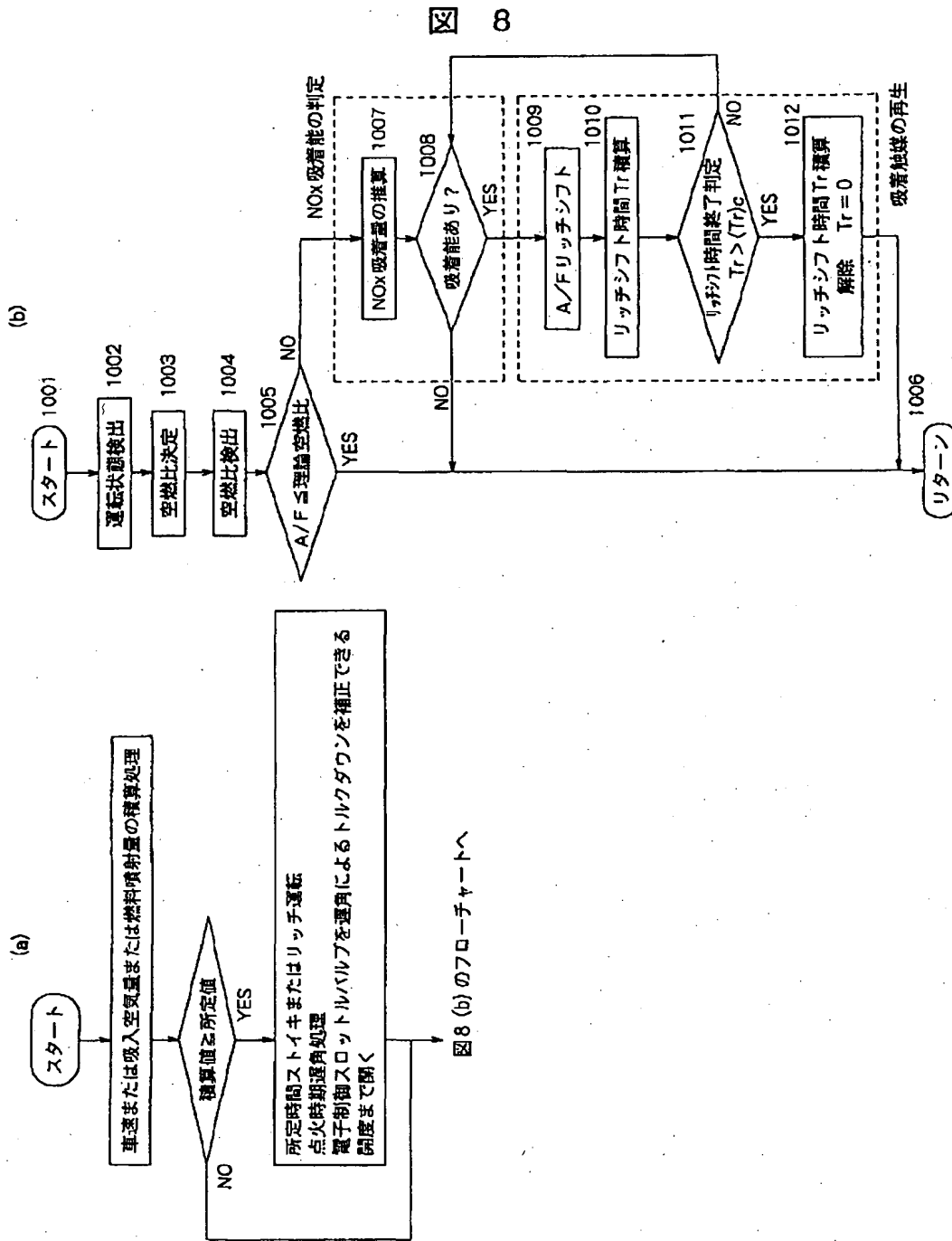


図 14

[Drawing 8]



[Drawing 15]

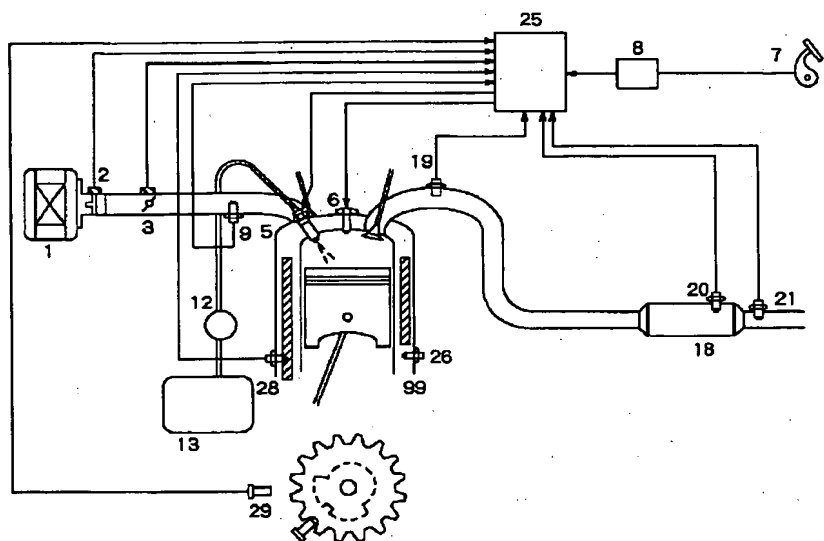


図 15

[Drawing 16]

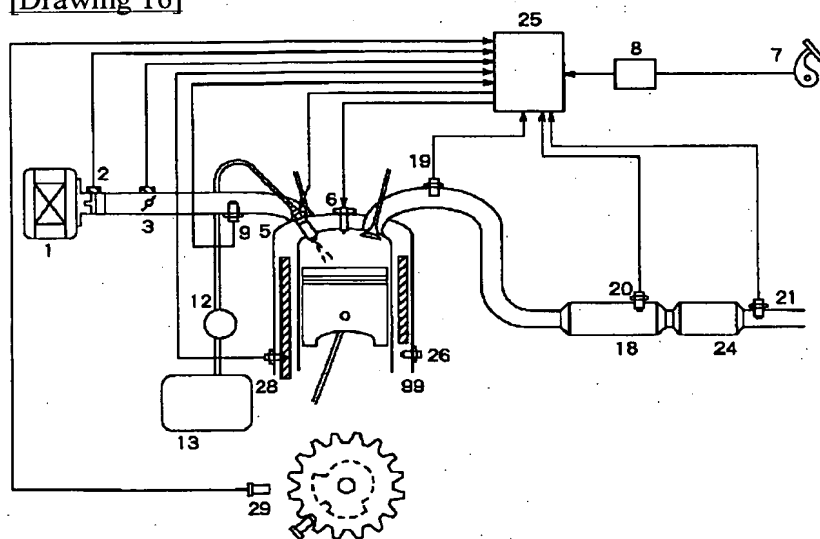


図 16

[Drawing 17]

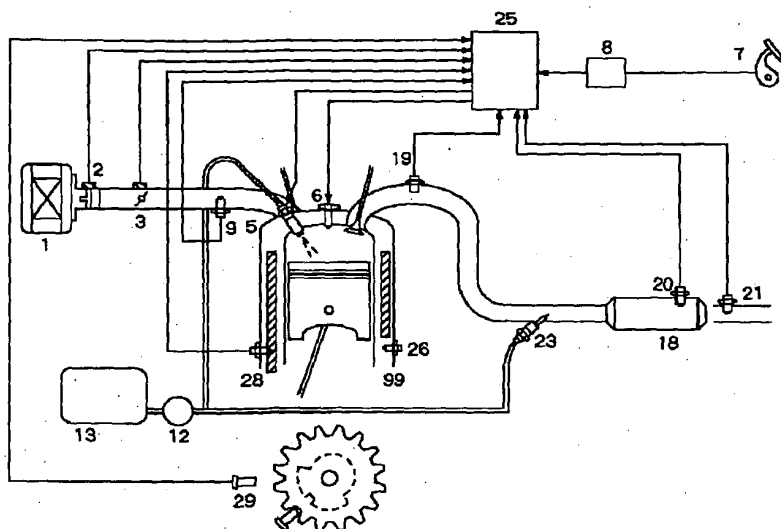
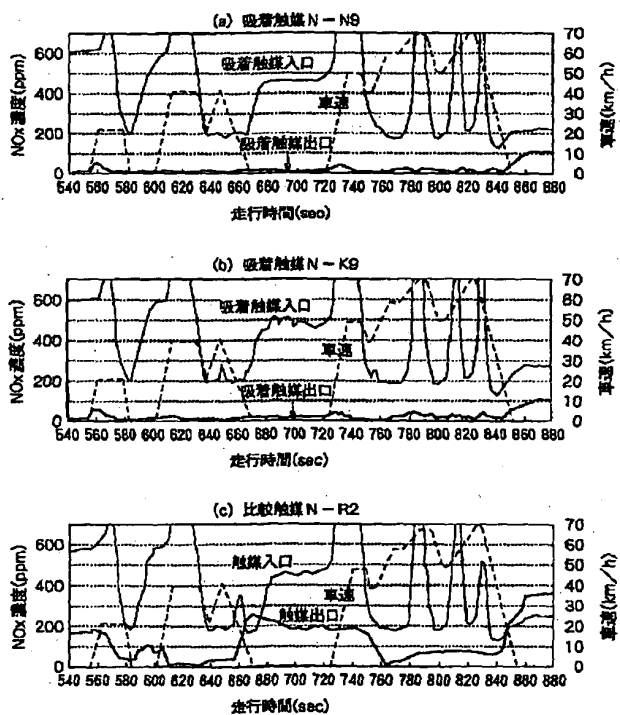


図 17

[Drawing 18]

図 18



[Translation done.]